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ON THE PEROXIDES AND SO-CALLED DOUBLE HALIDES.

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The double salts formed by the interaction of the halides of the alkali metals with those of the other metals generally, constitute an important and ever-growing class of substances which seem fully to deserve the qualification *homogeneous*.

If we except the recognition of the fact that the maximum number of molecules of alkali halide with which a given metallic halide interacts, is as a rule determined by the number of halogen atoms in the molecule of the metallic halide, we may say that the study of this class of bodies has not as yet resulted in any generalisation of importance.

While most chemists, to judge from the method of formulation usually adopted, seem to be in favor of the view that these double halides are representatives of the ill-defined and artificial class of molecular compounds, others maintain that they are true atomic compounds which owe their existence to the activity of the "residual affinities" of the chlorous atoms involved.

With regard to the former view, we fail to find any elucidation at all in the statement—double halides are molecular compounds. The inertia of scientific exploration is so great that it does not admit of any stoppage longer than is necessary to give more than a cursory glance at what is passed. If the nature of the phenomenon is not wholly revealed by this passing inspection, it is

relegated to a suspense-class for subsequent and more thorough investigation. It seems to us that the so-called molecular compounds constitute a suspense-class of this kind, which for convenience has received a mere name as distinguished from a connotation.

The explanation in terms of "residual affinities" is most gratuitous. Even were it preceded by a satisfactory description of the nature of an "affinity," it could not be regarded otherwise than as an ingenious and expiring effort of a theory now well to the west of its meridian. The admittance of the existence of residual affinities would in a measure account for the mere percentage compositions of a goodly number of the double halides, but it would at the same time most certainly lead us to wrong conclusions respecting their constitutions. If there is, as every one will we think readily admit, a universal correlation between structure and properties, then according to the doctrine of residual affinities the product of the interaction of $3KCl$ and $SbBr_3$ ought to differ in its behavior from the product of the interaction of $3KBr$ and $SbCl_3$. For the atom linking is different in the two cases. In both cases, according to the advocates of residual affinities, there is direct interaction between the bromine and chlorine atoms, but in the former case the chlorine atoms act only indirectly on the antimony atom, whereas in the latter case this action is direct. It is, however, a well ascertained fact that the products of the interaction of $SbCl_3$ and $3KBr$ on the one hand and $SbBr_3$ and $3KCl$ on the other, are identical.[1] Similarly the same body results from the interaction of TlI_3 and KI, as from the interaction of TlI and KI_3.[2]

Recently Mendeléeff[3] read a paper before the Royal Society in which he showed how the numerous carbon compounds, isomerides included, can be adequately represented quite independently of the valence theory and as a simple consequence of the application to the atomic constituents of molecules of Newton's Third Law of Motion in the form in which it appears when regarded as a corollary of the First Law. If the latter be true, then the internal stresses of any system must of necessity form a complete and mutual balance. This Law, coupled with a most plausible assumption, Mendeléeff introduces into chemistry under the title of the "Principle of Substitutions," which he illustrates much as follows:

[1] Atkinson: J. Chem. Soc. **43**, 290.   [2] Johnson: *Ibid.* **33**, 183.   [3] Nature 1032, 354.

Let ABC and AD represent two molecules; then since the interatomic stresses in these two molecules cannot have resultants, according to Newton's Third Law of Motion, it follows that the partial stress exerted (in some obscure way, in virtue, perhaps, of oscillatory or orbital motions) by A on BC is equal to the counter partial stress exerted by BC on A; that similarly the partial stress between A and D is exactly equal and opposite to that between D and A. Then comes the assumption—Mendeléeff calls it an axiom—which virtually states that the stress an atom exerts is constant for that atom; from which it follows at once that DBC will be a system in dynamic equilibrium, and therefore capable of existence.

It is the object of this paper to apply Mendeléeff's suggestion to what is known of the true peroxides [1] and double halides; and the outcome of this application, stated briefly, is that the members of this particular class of so-called double salts appear in the light of what by analogy may be called perhalide forms, bearing to the normal halides much the same relation as the true peroxides bear to the ordinary Group-oxides.

In dealing with the constitution of the peroxides, or rather their mode of derivation from the Group-oxides of Mendeléeff in terms of Newtonic principles, let us first briefly consider the simplest peroxides known, *viz.* those of hydrogen and potassium, and then pass on to those of Mendeléeff's eight Groups taken in order.

We might at first be inclined to regard hydrogen peroxide as derived from the water molecule H.OH by the substitution of the H atom of the hydroxyl group by hydroxyl itself, since, from the very fact of the existence of water, H and OH must be dynamically equivalent in the Newtonic sense. But on applying this mode of derivation to other stable hydroxides we get peroxides of higher degrees of oxidation than either are known to exist, or are probable. Thus sulphuric acid would yield the two peroxides SO_4 and SO_5; barium would form peroxides having the formulæ BaO_2 and BaO_3, whilst the lowest possible peroxide of potassium would be K_2O_3. Since, however, the highest known unequivocal peroxides of barium and sulphur have, respectively, the formulæ BaO_2 and S_2O_7, and the lowest peroxide of potassium is K_2O_2, it follows that we must reject unconditionally the view that peroxides may

[1] Mendeléeff has already made an incomplete application of his principle to a few of the better known peroxides.

empirically be regarded as formed by replacing the hydrogen atoms of the hydroxyls of the Group-hydroxides by hydroxyl, with subsequent dehydration.

But hydrogen peroxide may be derived from water in another way, which, although conducing to the same empirical result in the particular case of hydrogen peroxide as does the former method of attacking the problem, yet gives quite different results in the cases of the other peroxides.

Instead of conceiving a direct substitution of the hydrogen atom of the hydroxyl group by another hydroxyl group, let us glance at the results of supposing the hydrogen atom of the hydroxyl group substituted by the atom-complex constituted by all the remaining atoms in the molecule—a sort of reduplication or partial polymerisation with or without the elimination of water.

The application of this principle to the water molecule gives of course HO.OH. But there is no good reason for distinguishing between the hydrogen atoms in the water molecule, or for the assertion that one rather than the other is a constituent of the hydroxyl radicle. Hence it is probable that an elimination of one of the hydrogen atoms of hydrogen peroxide attended with a reduplication, will some day be realised in the isolation of a body H_2O_4[1] corresponding to its well known potassium analogue, K_2O_4.[2]

If we apply this principle of the derivation of the peroxides to what little is as yet known about the peroxides of the remaining Groups of the Periodic System, we find a close agreement between fact and deduction.

Hydroxides of Group II are of the type $M(OH)_2$. Hence peroxides of the elements of this group should exist of the types

$$M{<}^{OH}_{O} - {}^{HO}_{O}{>}M \quad \text{and} \quad M{<}^{O.O}_{O.O}{>}M.$$
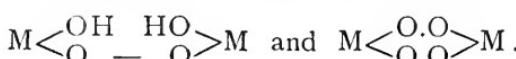
[1] Thénard and Berthelot are of the opinion that a peroxide of hydrogen of higher type than H_2O_2 is formed when $KMnO_4Aq$ and H_2O_2 interact at low temperatures.

[2] This form of reduplication seems to take place also in the case of hydrates of lower oxides than the highest Group-oxide. Thus P_2O_4 is the anhydride of hypophosphoric acid derived thus from phosphorous acid:

$$P(OH)_2O.H + P(OH)_2O.H \text{ gives } {}^{P(OH)_2O}_{P(OH)_2O}\} \text{ or } H_4P_2O_6.$$
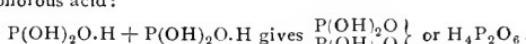
Sulphurous acid by the same method yields hyposulphuric acid, $H_2S_2O_6$, the anhydride of which is the alleged S_2O_5. S_2O_3 would be the anhydride of the reduplicated acid H_2SO_2 which Schützenberger thought to have prepared. Similarly N_2O_4 is derivable from nitrous acid. It is characteristic of all the oxides thus derived that they react with water to form, not the acids of which they are theoretically the anhydrides, but mixtures of other acids.

As representatives of the first type we have the bodies $Zn{}_O^{OHHO}{}_OZn$ and $Cd{}_O^{OHHO}{}_OCd$, usually written $Zn(OH)_2ZnO_2$ and $Cd(OH)_2CdO_2$ respectively. The well known peroxides of the alkaline earth metals are representative of the second type.[1]

The hydroxides of elements of Group III are of the general form $M(OH)_3$; these elements, in accordance with our views, should form peroxides having the empirical formulæ M_2O_4, M_2O_5 and M_2O_6. In the case of thallium, Tl_2O_4 is known in a state of combination; and the only other known peroxides of this group are the little-investigated bodies Y_4O_9 and La_4O_9.[2]

Peroxides of the elements of Group IV should exist having the compositions M_2O_5, M_2O_6, M_2O_7 and M_2O_8. Three of these types have known representatives in the bodies Zr_2O_5, Te_2O_6, Ce_2O_6, $Sn_2O_6.H_2O$ (?) and Th_2O_7.

Since the highest stable hydroxide of Group V is $MO(OH)_3$ —*i. e.*, $M(OH)_5$—H_2O,—the elements of this group should show

[1] It does not seem to have been incontrovertibly proved that barium dioxide is produced when the monoxide is heated in oxygen, text-books to the contrary notwithstanding. Brodie's results (Phil. Trans. 1850) seem to be the only quantitative ones in this connection, and they are not quite satisfactory. When the monoxide passes over into the peroxidised form, BaO_2, there should be a percentage increase of 10.5; whereas Brodie only found 7.56. Conversely, when the peroxide passes to normal oxide there should be a percentage loss of 9.5. Brodie found only 6.78. It should be here noted that the product of the interaction of barium oxide and potassium chlorate at a red heat is, according to Berthelot, not BaO_2 but Ba_2O_3, the dehydrated form of the first type $M{}_{\diagdown O.O\diagup}^{OH\ HO}M$. Thénard, the discoverer of a peroxide form of barium, had no quantitative analytical results, but merely conviction to adduce in favor of the formula BaO_2 (Ann. chim. phys. [2] 8, 308).

[2] Besides the peroxide forms deduced by the principle enunciated above, it seems necessary to admit others of intermediate type. Thus in addition to the two peroxides of potassium, K_2O_2 and K_2O_4, oxides having the compositions K_2O_3, K_4O_3, K_6O_4 and K_8O_5 have been described. Barium has also a peroxide form of the composition H_2BaO_4. Hitherto it has been customary to regard most of these bodies as "molecular compounds" of two oxides rather than as true atomic compounds. In accordance with this conception, these bodies are generally represented thus: $K_2O_2.K_2O = K_4O_3$; $K_2O_2.2K_2O = K_6O_4$; $K_2O_2.3K_2O = K_8O_5$; $BaO_2.H_2O = H_2BaO_4$. But they can be represented equally well in terms of Mendeléef's substitution theory without involving the idea of molecular combinations between peroxides, or between peroxides and normal oxides. Thus from BaO_2 we derive by substitution $Ba(OH)_2$ or $Ba(OH)O.H$. This in reacting with H_2O_2 or $(HO)O.H$, in accordance with Newtonian principles, gives $Ba_{(HO)O}^{(OH)O}$ or $BaO_2.H_2O_2$. The peroxide K_2O_3 may be similarly derived from K_2O_2 and H_2O_2, only in this case the reduplication is followed by dehydration. From the simultaneous existence of the compounds K_2O_3 and K_2O_2 we can predict the existences of the remaining peroxides of K. The peroxides M_4O_9 of Group III may in like manner be regarded as derived from what may be called the normal peroxides $M_2O_5[M_2O_4.O]$ and $M_2O_6[M_2O_5.O]$ thus: $_{M_2O_5}^{M_2O_4}$. The only objection is that this method of derivation does not seem to point to any limit in the number and complexity of the peroxides of a given element.

representatives of the types M_2O_6, M_2O_7 and M_2O_8. As yet, however, the only known peroxide of this group is N_2O_6.

The application of our principle to the stable hydrates of the Group-oxides of Group VI, $MO_2(OH)_2$, *i. e.* $M(OH)_6$—$2H_2O$, demands peroxides of the types M_2O_7 and M_2O_8.

The elements of this group show themselves particularly prone to the formation of peroxide forms, among which we may note S_2O_7 (both as anhydride, and in combination with bases as salts), Cr_2O_7 (?), Mo_2O_7 and W_2O_7 (both in combination with alkalies) and $UO_4.4H_2O$. The peruranates[1] of Fairley may most simply be regarded as hydrated bodies belonging to the same category as Schöne's H_2BaO_4 (see note 2, p. 5), *i. e.*, compounded peroxides formed in conformity with the substitution principle. Thus Na_4UO_8. $4H_2O = UO_4.2Na_2O_2.4H_2O$. Last year Traube[2] asserted that he had proofs of the existence of an oxide of sulphur SO_4, analogous in composition to the uranic peroxide just mentioned. But his proofs are not at all satisfactory,[3] and although according to the principles here developed SO_4 is a legitimate object of research, it seems as if Traube's sulphur holoxide were nothing else than Berthelot's persulphuric anhydride, S_2O_7.[4]

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[1] A thorough and more detailed investigation of these peruranates, and of peroxides generally, is much to be desired. More attention must henceforth be devoted to the determination of their constitution. There are many chemists who write $UO_4.4H_2O$ and $Na_4UO_8.4H_2O$ in the forms $U_2O_7.H_2O_2.7H_2O$ and $UO_6.2Na_2O.4H_2O$ respectively, with no better apparent reason for their procedure than that there is no room in their own private philosophies for bodies of the constitutions implied in the former formulæ. In terms of the idea of molecular compounds these methods of representation directly imply the existence of oxides U_2O_7, UO_6 and UO_4. The representation of a body in terms of the substitution principle does not in any way suggest the integral presence in the body of the constituents by whose interaction the body is presumably formed. Thus Fairley's peruranate, $Na_4UO_8.4H_2O$, regarded as the product of the interaction of $U(OH)_8$ [$= UO_4.4H_2O$] and $Na_2(OH)_2$ [$= Na_2O.H_2O$] would be represented thus: $$\left.\begin{array}{l} Na_2(OH).O \\ U(OH)_6.O_2 \\ Na_2(OH).O \end{array}\right\}\text{—See note 2, p. 5.}$$
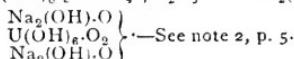
The other sodium peruranate described, *viz.* $Na_2U_2O_{10}.6H_2O$, may be regarded as similarly derived from $U_2(OH)_{14}$ [$= U_2O_7.7H_2O$] and $Na_2(OH)_2$ thus:

$$\left.\begin{array}{l} U_2(OH)_{12}O_2 \\ Na_2O_2 \end{array}\right\} = Na_2U_2O_{10}.6H_2O.$$
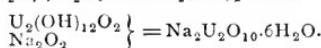
[2] Ber. d. chem. Ges. **24**, 1764.

[3] See Berthelot: Comp. rend. **112**, 1481; also Carnegie: Chem. News **64**, 1661.

[4] It has recently been stated (J. Chem. Soc. **59**, 785) that "the only result given by Traube which points to the possibility of such a substance (SO_4) being present in the oxidised liquid, is that showing the ratio of oxidising power to sulphuric acid formed on decomposition; the H_2SO_4 previously present having been removed by means of barium phosphate." But it seems to me that this ratio may be fully accounted for in terms of the equation of decomposition—

$$K_2S_2O_5 [= S_2O_7.K_2O] + H_2O = 2KHSO_4 + O$$
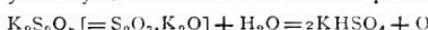
if we recall that it was *acidity* and not total sulphuric acid that Traube estimated.

The peroxides of Group VII should conform to the type MO_4, but as yet no peroxides of this group have been isolated.[1]

If considerations of symmetry and general plan are worth anything—and surely the results of reasoning based on the Periodic Law show that they are—then we are led to the conclusion that the elements of Group VIII will not form true peroxides. The highest stable hydrates of the oxides of elements belonging to Groups V, VI and VII are obtained by abstracting the elements of one, two and three molecules of water respectively from what we may call the orthohydroxides of these groups, in accordance with the following scheme :

	V.
Group	
Orthohydroxides,	$R(OH)_5$.
Stable hydrates,	$R(OH)_5 - H_2O = RO(OH)_3$.

	VI.
Group	
Orthohydroxides,	$R(OH)_6$.
Stable hydrates,	$R(OH)_6 - 2H_2O = RO_2(OH)_2$.

	VII.
Group	
Orthohydroxides,	$R(OH)_7$.
Stable hydrates,	$R(OH)_7 - 3H_2O = RO(OH)$.

Extending this regularity to Group VIII, *i. e.*, abstracting the elements of four molecules of water from its orthohydroxide, $R(OH)_8$, the result is a body altogether free of hydroxylic hydrogen, and therefore not amenable to the principles of peroxide derivation here developed. In strict conformity with these considerations we find that RuO_4 and OsO_4 are not only incapable of combining directly with water to form definite hydrates, but that their solutions in water do not exhibit any acid characteristics whatever.

It is worthy of note that this method of regarding the peroxides leads us to a conclusion which, though its significance is not yet very clear, has been repeatedly emphasised by Mendeléeff both in his Faraday Lecture of 1889, and in various connections in his " Principles of Chemistry," *viz.*, that a binary molecule *never* contains more than *four* atoms of oxygen per atom of the other constituent element.

[1] Franke thought to have prepared a peroxide of manganese MnO_4 in the form of a blue gas, but Thorpe and Hambly, following Franke's directions, were unable to obtain any evidence of a peroxide of manganese.

What, in conclusion, it may be asked, is the definition of a peroxide?

We would suggest, in answer, that all oxides of any given element with higher percentages of oxygen than the highest Group-oxide of the element according to Mendeléeff, are true peroxides.[1] Mendeléeff to the contrary, such peroxides may be possessed of truly basic or acidic properties; some may even be anhydrides. Thus, S_2O_7 is the anhydride of an acid $H_2S_2O_8$ which forms salts (isolated by Marshall) by replacement of the two hydrogen atoms by metals. The same, according to Péchard, is true of Mo_2O_7 and W_2O_7.[2] Other peroxides such as UO_4 do not appear to be truly anhydrides—that is, they do not form hydrates with replaceable hydrogen. Yet they have something akin to acid properties, in virtue of which they form compounds with the peroxides of the more basylous metals. When one recollects that it is impossible sharply to differentiate such classes as metals and non-metals, acids and bases, etc., it is not to be wondered at that the diagnosis of peroxides from their properties alone is not a sharply defined one. As a class they may be said to be less stable at high temperatures than the normal oxides. They are for the most part decomposed by water and very dilute acids, and it is probable that a more careful examination of these decomposition-products will in all cases disclose the presence of hydrogen peroxide. Many of these bodies when treated with concentrated sulphuric or nitric acid disengage ozonised oxygen, and this reaction is very probably a distinctive reaction of the class.

Before passing on to the so-called double halides formed by the alkali metals, we must first glance at the perhalide forms of the alkali metals themselves.

From the molecules KO.H and HO.H we get, by the principle of substitutions, KO.OH in which the oxygen atoms bear the same relation to each other that they do in peroxide of hydrogen. They may therefore be substituted by two hydrogen atoms giving us KH.HH. But the hydrogen atom is equivalent from a substitution point of view to a halogen atom, say I; and thus we arrive at the well known triiodide of potassium, KI_3. Although

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[1] Hence PbO_2, MnO_2 and CrO_3 are not true peroxides.

[2] Cammerer (Chem. Zeit. **15**, 957) accepts the formula $2MoO_3.H_2O_2.xH_2O$ in preference to Péchard's formula $H_2Mo_2O_8.xH_2O$. Cammerer has also isolated a peroxide of tungsten which he represents as $WO_5.H_2O_2.H_2O$. But there seems to be no good reason why it should not be represented as a hydrate of the theoretically-possible tetroxide, $WO_4.2H_2O$.

solubility-data point to the probable existence of analogous bromine and chlorine compounds of potassium, these have not yet been isolated. Quite stable bodies of the type MX_3 (where X is any halogen) have, however, recently been described where M is cæsium.

From the existence of a chloride of iodine having presumably the molecular formula ICl_3, still higher perhalide compounds of the alkali metals are possible, and are known. By the principle so often employed already, $KI_2.I + Cl_2.I$ points to the existence of a body $KI_2.Cl_3$, or in general to bodies of the type KX_5. Wells and Wheeler have described, among others, the following substances conforming to this type: CsI_5, $CsBr_5$, $KCl.Cl_3I$, $LiCl.Cl_3I$.

Since, however, of the three iodine atoms in KI_3 two bear necessarily a similar relation to the system, no reason exists why a further substitution should not take place between the two molecules KI_2Cl_3 and ICl_3 giving us (say) $KICl_3.Cl_3$, or in general a body of the type KX_7. Such a body is known in the double fluoride KH_3F_4—usually written $KF.3HF$. It must be noted that no double halide of alkali metal and hydrogen of higher type than this is known.

Passing on now to the elements of Group II, whose stable hydroxides are of the form $M(OH)_2$. By the substitution principle,

$$M{\scriptstyle{OH \atop O.}}H + KO.H \text{ gives } {\scriptstyle MO \atop KO}\Big\}{\scriptstyle OH}.$$
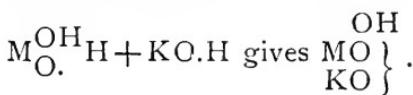
This by reason of the existence of $\Big\{{\scriptstyle OH \atop OH}$ gives $M{\scriptstyle OH \atop K}{\scriptstyle \atop H}\Big\}{\scriptstyle H}$, and this

MX_3K, where X is any halogen atom, and M an element belonging to Group II. Of the many bodies conforming to this type we shall take the single example $MgF_2.NaF$.

$$\text{But } M{\scriptstyle O.H \atop H \atop KH}\Big\} + KO.H \text{ gives } M{\scriptstyle KO \atop O \atop H \atop KH}\Big\}\text{ ; and this, as before, } M{\scriptstyle KH \atop H \atop H \atop KH}\Big\}\text{ or}$$
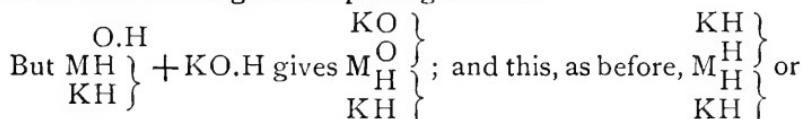
MK_2X_4. Again we shall take but one example of the many bodies of this type, $BeCl_2.2KCl$.

Finally, by four successive substitutions on Newtonic principles between MK_2X_4 and the halide atoms of 4 molecules of KX_3— one atom from each molecule—we arrive at the perhalide types MK_3X_5, MK_4X_6, . . . MK_6X_8. As yet, however, representa-

tives of only the first two types are known—*e. g.*, $ZnCl_2.3NH_4Cl$; $CdCl_2.4KCl$. It would seem therefore that higher perhalide forms of the elements of Group II remain to be discovered.

Similar reasoning applied to Group III leads to the following gamut of perhalide types for the elements of this group:

$$MKX_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad AlCl_3.NaCl$$
$$MK_2X_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad AlF_3.2NaF$$
$$MK_3X_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad AlF_3.3NaF$$
$$MK_4X_7 \quad . \quad . \quad . \quad . \quad . \quad . \quad \ldots$$
$$MK_5X_8 \quad . \quad . \quad . \quad . \quad . \quad . \quad TlI_3.5TlI[1]$$
$$\quad \cdot$$
$$\quad \cdot$$
$$MK_9X_{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad \ldots$$

Group IV is especially rich in perhalide compounds, which according to theory should range between the limits MKX_5 and $MK_{12}X_{16}$ for the "-ic" salts, and the limits MKX_3 and MK_6X_8 for the "-ous" salts.

$$MKX_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad ZrF_4.KF$$
$$MK_2X_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad ThF_4.2KF$$
$$MK_3X_7 \quad . \quad . \quad . \quad . \quad . \quad . \quad TiCl_4.3NH_4Cl$$
$$MK_4X_8 \quad . \quad . \quad . \quad . \quad . \quad . \quad [ZrF_4.2CdF_2]$$
$$MK_5X_9 \quad . \quad . \quad . \quad . \quad . \quad . \quad \ldots$$
$$MK_6X_{10} \quad . \quad . \quad . \quad . \quad . \quad TiCl_4.6NH_4Cl$$
$$MK_7X_{11} \quad . \quad . \quad . \quad . \quad . \quad \ldots$$
$$MK_8X_{12} \quad . \quad . \quad . \quad . \quad . \quad ThCl_4.8NH_4Cl$$
$$MK_9X_{13} \quad . \quad . \quad . \quad . \quad . \quad PbCl_4.9NaCl$$
$$\quad \cdot$$
$$\quad \cdot$$
$$MK_{12}X_{16} \quad . \quad . \quad . \quad . \quad . \quad \ldots$$

$$MKX_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad SnBr_2.KBr$$
$$MK_2X_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad PbI_2.2KI$$
$$MK_3X_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad PbI_2.3NH_4Cl$$
$$MK_4X_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad PbI_2.4KI[2]$$
$$MK_5X_7 \quad . \quad . \quad . \quad . \quad . \quad . \quad \ldots$$
$$MK_6X_8 \quad . \quad . \quad . \quad . \quad . \quad . \quad PbBr_2.6NH_4Br.$$

[1] The thallium atom is, we know from the existence of thallous compounds, substitutionally equivalent to the atom of an alkali metal.

[2] Doubt has been thrown on the existence of Boullay's $PbI_2.4KI$ by Remsen and Herty: This Journal **11**, No. 5; **14**, No. 2.

In connection with the double halides formed by the plumbous salts occurs the only discrepancy between theory and actuality that we have met in the course of this review. According to theory, MK_6X_8 should define the limit for plumbous perhalides, and all perhalides of higher type than MK_4X_6 we would expect to be quite unstable. But André claims to have separated homogeneous and fairly stable compounds having the empirical formulæ $PbX_2.7NH_4X - PbX_2.10NH_4X$. This discrepancy merits a more careful experimental investigation.

The elements of Group V form very few perhalide compounds; the known representatives are all of low type, and fall well within the limits assigned by theory—*e. g.*, $BiCl_3.2NaCl$; $BiCl_3.3NH_4Cl$; $BiCl_3.4NH_4Cl$. Scarcely anything is known concerning the double alkali halides formed by the more basic elements of Group VI ; and the important perhalides of the elements of Group VIII are all normal, but of very low type.

A review of these perhalides and their mode of derivation suggests a subdivision into three groups, *viz.*, perhalides of the first, second, and third orders.

To the first order belong those perhalides which, from a molecular-compound standpoint, do not contain a greater number of molecules of alkali halide than the number of halogen atoms in the molecule of the other metallic halide involved. To this order belong such bodies as $MgF_2.NaF$ and $BeCl_2.2KCl$. The ability to form the limit-compounds of this order is possessed in higher degree by the elements of the lower groups than by those of the higher. Of the many important perhalides formed by the tetra-halides of the metals of Group VIII—the platinum group of metals—none reach the limit form $MX_4.4KX$.

The second order is composed of those perhalides which may be regarded as containing a number of alkali halide molecules anywhere between the number limiting the first order and double that number—*e. g.*, $ZnCl_2.3NH_4Cl$; $CdCl_2.4KCl$.

Finally, the third order comprises those perhalides which contain a number of alkali halide molecules ranging between the number limiting the second order and three times the number limiting the first order. Such, for instance, are the bodies $BaCl_2$, $5KCl$ and $BaCl_2.6KCl$ yet to be discovered. Group IV, however, furnishes us with an example of this order in the body $PbBr_2.6NH_4Br$.

It is particularly noteworthy that the great majority of the known perhalides belong to the first order, and that ammonium halides seem more prone to form perhalides of higher orders than do the halides of the alkali metals. Or at least we may say that as the order rises the stability of the perhalide decreases, but that this decrease of stability appears to be less for the ammonium halides than for the alkali metal halides.

In addition to the perhalides already noticed in this paper, numerous intermediate, or poly-, halides are possible and are known to exist—*e. g.* :

$2CeF.3KF$; $2BiI_3.3NaI$; $3MoCl_4.2KCl$; $2HgCl_2.KCl$, etc.

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ON THE LIBERATION OF NITROGEN DURING PUTREFACTION.

BY HOWARD B. GIBSON.

Historical.—The study of the conditions and processes which affect the supply of combined nitrogen has been a very fruitful one, and the brilliant researches which led to the discovery that the leguminæ utilise free nitrogen by a process of symbiosis with certain micro-organisms, are too widely known to need more than passing notice. While the supply of combined nitrogen may be increased in this way, and probably in others, there are also processes continually going on by which combined nitrogen passes into the free state ; among them may be mentioned the use of our modern explosives, the combustion of organic nitrogenous substances, and the action of certain micro-organisms in the process of putrefaction.

The study of the liberation of nitrogen during putrefaction was begun by Rieset[1] in 1856, and has been continued until the present day with very varied results. Between 1856 and 1882 Lawes, Gilbert and Pugh,[2] in England, and Koenig,[3] Morgen,[4] Dietzell,[5] and Gautier and Etard,[6] in Germany and France, conducted

[1] Compt. rend. 1856, 63.   [2] Phil. Trans. Lond. 1861, 497.
[3] Der Kreislauf des Stickstoffs, Münster, 1878.   [4] Landw. Vers.-Stat. **30**, 199.
[5] Ber. d. chem. Ges. **16**, 551.   [6] Compt. rend. **94**, 1357.

experiments which showed that liberation of nitrogen may take place. Since 1882 experiments by Ehrenberg,[1] Tacke,[2] Kelner and Yoshii,[3] Schlösing,[4] and Berthelot and André[5] have given negative results, while in further researches by Tacke[6] and also by Immendorff[7] positive results have been obtained.

In these experiments two general methods have been followed : the " difference " method, in which the nitrogen in a definite amount of substance is determined before and after putrefaction ; and the " gas-analysis " method, in which the gaseous products of putrefaction are examined for the presence of nitrogen gas. Both methods, as formerly used, are open to criticism, the former because of the possibility of the passage of indol, skatol, etc., through the solutions used in absorbing the ammonia gas formed during putrefaction, and of the loss of volatile nitrogenous substances while drying the residue preparatory to analysis ; and the latter because the conditions of experiment are apt to be abnormal. The absence of the details of much of the work previous to 1882, in which the "difference" method was almost exclusively used, makes it impossible to estimate the extent to which errors of method may have influenced results, but in much of the work by the " gas-analysis " method the conditions of experiment have been such as to render results of a very questionable nature.

The classification of such a mass of results along definite lines is difficult, especially in the case of the work previous to the last five years; but in the more recent work, with a single exception observed by Immendorff, no losses of nitrogen have occurred when nitrates have not been found present at the end of the experiment, although the presence of nitrates has often been observed when no liberation of nitrogen has taken place. Two principal theories have been advanced in explanation of the liberation of nitrogen. The older one, adopted by Koenig and Morgen, was that the ammonia formed in putrefaction was oxidised to nitrogen gas and water in a manner analogous to the decomposition of ammonia gas by chlorine. In the later theory the liberation of nitrogen has been associated with the process of nitrification, in connection with which, as mentioned above, the liberation of nitrogen has been observed. The evidence as to a direct con-

[1] Ztschr. physiol. Chem. **11,** 145, 438.   [2] Landw· Jahrb. **16,** 917.
[3] Ztschr· physiol· Chem· **12,** 95·
[4] Compt· rend., **108,** 261 ; Ref.—Centrbl· Agr.-Chem. 1889, 218·
[5] Compt· rend· **114, 5**14·   [6] Landw· Jahrb. 1889, 39·   [7] *Ibid.* 1892, 281·

nection between the two processes seems to be negative. Neither Ehrenberg[1] nor Schlösing[2] observed liberation of nitrogen during the nitrification of ammonium salts in presence of oxygen.

Dehérain[3] observed a loss of nitrogen in soil in which nitrification was going on, but he did not refer the loss to nitrification itself, as the loss did not occur until the intensity of the nitrification process had begun to decrease. Tacke's[4] experiments by the difference method showed gain as well as loss of nitrogen where nitrification had taken place, and Immendorff[5] observed a loss in all cases when nitrification had gone on, but failed to discover any quantitative relation between nitrification and loss of nitrogen. Leone[6] observed the reduction of nitrates by micro-organisms, and E. Bréal[7] has found an aerobic ferment which reduces nitrates to free nitrogen.

This evidence as a whole, and especially the observations of Leone and Bréal, seems to indicate that the liberation of nitrogen is a process independent of nitrification.

In two of Immendorff's experiments heavy losses of nitrogen occurred without either nitrates or nitrites being present at the end of the experiments. There is nothing in this experimental work, however, which debars the possibility of previous nitrification and reduction, but Immendorff takes the ground that liberation of nitrogen may be caused by the action of micro-organisms independent of the process of nitrification. Although Immendorff's experimental work may not entirely justify his conclusions, the writer believes this theory is correct, and offers his own experimental work as proof that the liberation of nitrogen may take place during putrefaction, without the previous formation of either nitrates or nitrites.

Method.—In the experimental work herewith reported, simplicity of method was the end ever kept in view. The "differrence" method was used, and the substance experimented upon was allowed to putrefy in glass bell-jars varying in size from one to three liters, and was placed in small watch-glasses arranged on metal stands. As none of the portions in the several glasses exceeded one gram in weight, the access of air to the putrefying mass was much freer than would have been possible had the substance been in a single large portion. Washed air was passed

[1] Ztschr. physiol. Chem. **11**, 446.   [2] Compt. rend. **109**, 423.
[3] Centrbl. Agr. Chem. 1887, 728.   [4] Landw. Jahrb. 1889, 39.
[5] *Ibid.* 1892, 281.   [6] Centrbl. Agr.-Chem. 1890, 283.   [7] Compt. rend. **114**, 681.

through the jars—as a rule every day—at the rate of about 4 bubbles per second. The average daily quantity of air thus passed through each jar was approximately equal to twice its capacity. Before admission to each jar the air was thoroughly washed by dilute aqueous solutions of caustic soda and sulphuric acid in order to remove all traces of nitric or nitrous acid and ammonia which it might contain. On leaving the bell-jar the air was made to pass, in the experiments of Series 1, through a dilute solution of sulphuric acid to absorb the ammonia formed during putrefaction; and, in Series 2, through concentrated sulphuric acid to absorb indol, skatol, etc., as well as ammonia.

The substances under treatment were lean beef and blood serum which in air-dried condition showed approximately the following composition :

Lean beef.—Water, 4.8 ; ash, 4.2 ; ether extract, 15.2 ; nitrogen, 12.0 per cent.

Blood serum.—Water, 10.7 ; ash, 10.0 ; nitrogen, 11.8 per cent.

The nitrogen content was carefully determined at the beginning of each experiment and, at its close, that of the several residues, which were transferred directly to the Kjeldahl digester without drying. Comparison of the original nitrogen content with that of the several residues *plus* the nitrogen found in the absorption-apparatus and water with which the jar and its fixtures had been carefully washed at close of experiment, showed whether liberation of nitrogen had taken place.

Error.—The errors especially guarded against were introduction of combined nitrogen in the air used in ventilation, loss of indol, skatol, etc., and leakage. As stated above, the air was thoroughly washed before admittance to the jars. In Series 2, indol, skatol, etc., were held back by the use of concentrated, instead of dilute, sulphuric acid in the absorption-apparatus, which was heated from time to time to decompose the absorbed gases. It was found that the use of concentrated acid prevented the escape of ill-smelling gases, which was very noticeable in Series 1, and discoloration of the acid was observed when the gases were allowed to pass through it on several successive days without heating. Each jar was carefully tested before each experiment and found capable of resisting a pressure from within equal to about 2 cm. of mercury. The use of a simple automatic device, however, excluded the possibility of pressure from within, and the possibility of error from leakage was thus practically excluded.

Although analytical errors are by no means a complete estimate of the error of a series of experiments of this kind, it may not be out of place to state that in the writer's use of the Kjeldahl method of nitrogen determination, which was used exclusively, the incidental error of titration rarely, if ever, exceeded 0.05 cc. of the alkaline solution, or less than 0.2 mg. of nitrogen. The probable error of the six series of determinations by which the original nitrogen content of the substances under experiment was found was ± 0.2, ± 0.1, ± 0.3, ± 0.3, ± 0.2, ± 0.4 mg. of nitrogen, respectively. Of the 34 individual determinations of the six series but a single one was rejected.

Conditions of Experiment.—The putrefaction was allowed to proceed in atmospheric air in very large excess of the actual amount necessary for the oxidation of the substance undergoing decomposition. No special effort was made to regulate the temperature at which the putrefaction took place, and the temperature of the laboratory ranged from 6° or 8° to 25°, and often changes of 12° or 15° occurred within 24 hours during the winter months. Distilled water was added to all portions of the substance at the rate of from 2 to 6 cc. of water per gram of substance. In Experiments 1–6 the putrefaction was started by addition of a drop of very dilute emulsion of putrid meat, and in Experiments 7–9 a couple of drops of dilute soil infusion were added in addition to the inoculation with the meat. With the exception of the manner of inoculation, all the experiments were carried on under approximately the same conditions. Neither the emulsion of meat nor the soil infusion contained a determinable amount of nitrogen per cc.

In the following table special attention is called to the loss per day both in milligrams, and in percentage of nitrogen taken, which brings out the following three points: (1) the comparative regularity of loss per day in Series 1; (2) smallness of loss in Experiment 6, in which, as in all experiments of Series 2, concentrated sulphuric acid was used in the absorption-apparatus, in comparison with losses in Series 1, where dilute acid was used; (3) difference in loss between experiments inoculated with soil infusion (7, 8 and 9) and the others.

The last column cannot be taken as an exact measure of the extent of the ammoniacal fermentation, as only total nitrogen was determined in the residues after putrefaction.

A TABLE SUMMARISING ALL RESULTS.

Series.	Number.	Substance.	Inoculation.	Duration of Experiment in Days.	Nitrogen taken (in grams).	Nitrogen found (in grams).			Loss.				Nitrogen in Absorption-apparatus and Wash-water, in Percentage of Nitrogen taken.
						In Residue.	In Absorption-apparatus and Wash-water.	Total.	Total.		Per Day.		
									In Milligrams.	In Percentage of Nitrogen taken.	In Milligrams.	In Percentage of Nitrogen taken.	
1	1	Beef.	Putrid Flesh.	63	0.6026	0.5058	0.0909	0.5967	5.9	1.0	0.09	0.016	15
1	2	Blood Serum	"	167	0.5934	0.3372	0.2302	0.5674	26.0	4.4	0.16	0.026	39
1	3	"	"	168	0.5943	0.4031	0.1739	0.5770	17.3	2.9	0.10	0.017	29
1	4	"	"	87	1.0717	0.8383	0.2158	1.0541	17.6	1.6	0.20	0.018	20
1	5	"	"	98	1.0245	0.7456	0.2643	1.0099	14.6	1.4	0.15	0.014	26
2	6	Beef.	"	126	0.6057	0.5223	0.0762	0.5985	7.2	1.2	0.06	0.010	13
2	7	"	Putrid Flesh and Soil Infusion.	122	1.0283	0.4394	0.4350	0.8744	153.9	15.0	1.26	0.123	42
2	8	"	"	84	1.0334	0.7252	0.1865	0.9117	121.7	11.8	1.45	0.140	18
2	9	"	"	82	1.0290	0.7621	0.1682	0.9303	98.7	9.6	1.20	0.117	16

Theoretical Conclusions.—In Experiments 1, 4, and 5, a single representative portion, the nitrogen content of which was assumed from the average of the remaining ones, was tested for the presence of nitrates and nitrites by the starch-paste test, but with negative results. In Experiment 2, three portions, and in Experiment 3 all the portions, were tested by the diphenylamine test, but also with negative results.[1] In Series 2 each portion of each experiment was tested by the diphenylamine test, but not the slightest trace of nitrates or nitrites was detected. The possibility of nitrification and subsequent reduction is excluded, as Experiments 8 and 9 serve as control-experiments on Experiment 7 in the following manner: The duration of Experiments 8 and 9—84 and 82 days respectively—is only two-thirds that of Experiment 7—122 days—and, as the loss of nitrogen is directly proportional to the length of the experiment, therefore, if liberation of nitrogen had taken place at the same time with, or directly following, the nitrification process, nitrates would have been present in Experiments 8 and 9. Further, in each experiment the rate of putrefaction in the several portions varied very widely, so that the individual portions—of which there were 16 in each experiment—act as a control on each other and on the experiment as a whole. Bearing these facts in mind, the writer does not hesitate to assert that liberation of nitrogen without the previous formation of nitrates or nitrites may take place during the process of putrefaction as a result of the action of micro-organisms.

Summary.—1. Liberation of nitrogen may take place during the process of putrefaction.

2.—In the experiments reported, the liberation of nitrogen has been dependent on the inoculation, and certain micro-organisms (found in the putrid flesh) seem incapable of carrying on this process in any marked degree, while others (found in the soil infusion) have caused a marked loss of nitrogen.

3.—The micro-organisms have produced liberation of nitrogen independent of the process of nitrification.

In conclusion, the writer acknowledges his deepest obligation to the advice and kindness of his honored instructor, Professor Dr. F. Stohmann, under whose direction this research was carried on.

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[1] In the diphenylamine test the amount of substance required for the test was not large enough to be taken into quantitative consideration.

A STUDY OF CALIFORNIA PETROLEUM.

PRELIMINARY NOTICE.

BY FELIX LENGFELD AND EDMOND O'NEILL.

Petroleum occurs in many localities in California, most abundantly in the southern part, especially in Ventura and Los Angeles counties.

The industry has reached considerable proportions, the amount produced in 1888 being 704,619 barrels (of 42 gallons each[1]), and the annual yield is now probably much more than that amount.

The knowledge of its occurrence dates back many years; even as early as 1851 it was being distilled on a small scale, and in 1857 a comparatively large plant was erected in Santa Barbara county.

In 1865 there were 65 companies with a nominal capital of $45,000,000 engaged in the oil industry.[2] Interesting and full information on the subject is contained in the various reports of the California State Mining Bureau, especially those of 1884, 1887 and 1890. In spite of the above facts but little appears to have been done towards investigating the chemical nature of California petroleum.

In 1867 Silliman made rough analyses of some California oils, determining the specific gravity of a few fractions and giving the result of "cracking."[3] In 1887 W. C. Johnston determined the specific gravity of 16 samples, then distilled them and determined the amount and the specific gravity of fractions taken every 50° up to 300°.

With the exception of the above, we have been unable to find anything more than a passing allusion to California petroleums. Believing a systematic investigation would prove of value, we have undertaken it with that idea in view.

The oil was furnished us by the Pacific Coast Oil Company and came from Pico Cañon, in the San Fernando mountains, Los Angeles county, at present the most productive field in the State.

The crude petroleum is thick, and dark-green in color, with a specific gravity of 0.8414 at 15° C. and a refractive index of 1.4810 at 14° C. About 18 liters of the crude oil was subjected

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[1] Min. Res. of the U. S., Sixth Report.   [2] Fourth Ann. Rep. Cal. Min. Bur., p. 295.
[3] Am. Jour. Sci., pp. 43-242.

to fractional distillation, collecting at every ten degrees, each fraction redistilled, collecting at every five degrees, and this repeated for every fraction from three to five times. A very small quantity came over below 40°. When the temperature reached 200° the distillation was conducted under diminished pressure, but the final fractions were obtained under atmospheric pressure, and the temperatures given are at normal pressure. The lower fractions were water-white; the higher, slightly colored and possessed a marked fluorescence. A tendency to collect in larger amounts at 75°–85°, 150°–160°, 190–200° and 240°–250° was observed, but in general the fractions were nearly uniform in amount.

The refractive index and specific gravity of each fraction are given in the following table; the latter was determined with a Westphal balance at a temperature of 15°, the former with an Abbé refractometer.

Boiling-point of Fractions.	Specific Gravity.	Refractive Index.	Boiling-point of Fractions.	Specific Gravity.	Refractive Index.
Below 40°	0.6344	1.3669	180–185	0.8005	1.4451
40–50	0.6545	1.3760	185–190	0.8030	1.4464
50–60	0.6724	1.3846	190–195	0.8062	1.4482
60–65	0.6882	1.3900	195–200	0.8096	1.4500
65–70	0.6996	1.3924	200–205	0.8126	1.4519
70–75	0.7108	1.3982	205–210	0.8153	1.4531
75–80	0.7195	1.4020	210–215	0.8194	1.4553
80–85	0.7278	1.4065	215–220	0.8220	1.4572
85–90	0.7340	1.4090	220–225	0.8268	1.4600
90–95	0.7388	1.4111	225–230	0.8308	1.4621
95–100	0.7433	1.4134	230–235	0.8340	1.4650
100–105	0.7475	1.4165	235–240	0.8391	1.4678
105–110	0.7507	1.4185	240–245	0.8430	1.4699
110–115	0.7533	1.4203	245–250	0.8460	1.4720
115–120	0.7570	1.4222	250–255	0.8498	1.4741
120–125	0.7598	1.4245	255–260	0.8516	1.4760
125–130	0.7635	1.4291	260–265	0.8527	1.4771
130–135	0.7675	1.4301	265–270	0.8549	1.4780
135–140	0.7680	1.4299	270–275	0.8556	1.4787
140–145	0.7719	1.4327	275–280	0.8587	1.4791
150–155	0.7786	1.4344	280–285	0.8595	1.4794
155–160	0.7820	1.4362	285–290	0.8612	1.4795
160–165	0.7855	1.4382	290–295	0.8630	1.4804
165–170	0.7897	1.4404	295–300	0.8649	1.4824
170–175	0.7934	1.4421			
175–180	0.7967	1.4440	Original oil, 0.8414		1.4810

The fractions boiling below 110°, when treated with a mixture of nitric and sulphuric acids until no further action took place, gave a liquid heavier than water, that resembled nitrobenzene in smell and general appearance, but, on attempting to distil it, a sudden decomposition took place. The same thing has been observed in this laboratory in attempting to prepare nitrobenzene from impure benzene; a liquid having the general properties of nitrobenzene is produced, but cannot be distilled without decomposition. A preliminary examination of these fractions shows that the oil contains paraffins, naphthenes, and benzene-homologues, and is apparently intermediate in composition between the Pennsylvanian and Russian petroleums.

A complete chemical investigation of this petroleum is being carried on in this laboratory, and we should therefore like to reserve the field for the present.

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SOLUBLE PENTOSES IN PLANTS.

BY G. DE CHALMOT.

It has recently been recognised that among the substances occurring most widely distributed in plants are the pentosanes (Tollens),[1] which yield pentoses by hydrolysis and, in many cases, form a considerable part of plants. Tollens and his students found more than 20 per cent. in different kinds of straw, and, later, Flint[2] found as much as 30 per cent. in beech wood and corn stubble.

The sugars which have up to the present time been obtained from these pentosanes are arabinose and xylose. The arabinose-carbonic acid obtained by Kiliani[3] by the action of hydrocyanic

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[1] Scheibler: Ber. d. chem. Ges. **1**, 58, 108; **6**, 612. R. W. Bauer: J. prakt. Chem. [2] **34**, 47; **43**, 112. Poumarède and Figuier: J. prakt. Chem. [2] **12**, 29. Th. Thompson: Ber. d. chem. Ges. **13**, 2168. F. Koch: Ber. d. chem. Ges. **20**, 145. Tollens, Wheeler, Allen, Günther, DeChalmot: Landw. Vers-Stationen **39**, 401. K. Bieler: Inaug. Diss. (Göttingen, 1890). Stone: Ber. d. chem. Ges. **23**, 3791; **24**, 1657. E. Schulze: Ber. d. chem. Ges. **23**, 3110; **24**, 2270. Winterstein: Ber. d. chem. Ges. **25**, 1237. A. Voswinkël: Pharm. Centrbl. [N. F. VIII] **36**, 505. C. Lintner and G. Dull: Ztschr. angew. Chem. 1891, 538.

[2] Ed. Flint: Inaug. Diss. (Göttingen, 1892).

[3] Ber. d. chem. Ges. **20**, 345.

acid on arabinose was found by Emil Fischer[1] to be identical with
l.-mannonic acid; and it was also shown that besides the *l.*-mannonic
acid some *l.*-gluconic acid was formed in the reaction. The carbon
atoms 2 to 4 in arabinose are stereo-isomeric with those in
l.-mannose and *l.*-glucose, a fact which is best shown by the use
of Fischer's formulæ.

	Arabinose.	*l.*-Mannose.	*l.*-Glucose.
6		C.OH	C.OH
5	C.OH	H—C—OH	HO—C—H
4	H—C—OH	H—C—OH	H—C—OH
3	HO—C—H	HO—C—H	HO—C—H
2	HO—C—H	HO—C—H	HO—C—H
1	CH₂OH	CH₂OH	CH₂OH

Fischer[2] also proved that xylose-carbonic acid is the isomer of
d.-gluconic acid, which had been obtained by him by the reduction
of *d.*-gluco-saccharic acid, and that, therefore, xylose is a laevo
compound. All other sugars which have been extracted from
plants belong to the dextro series. Now one has either to con-
sider that the plants possess the power of changing dextro sugars
into laevo sugars, or that, besides the dextro sugars, laevo sugars
are formed by the assimilation-process.

In the first case a decided change would have to take place ;
but with regard to the second, Emil Fischer[3] and others have
referred to the fact that in the artificial formation of compounds
with asymmetrical carbon atoms, an equal number of molecules
of the dextro and laevo varieties were almost always formed.

He supposed that if in plants we generally found active sub-
stances only, it was because the plants had transformed the
isomers into some other substances. Baeyer's theory, according
to which plants form carbohydrates from formaldehyde, has
lately received strong support from two directions. (1) Fischer
showed that there were two sugars of the composition $C_6H_{12}O_6$ in
the formose prepared by Löw[4] from formaldehyde, and that that
one of these which occurred in small quantities only was identical

[1] Ber. d. chem. Ges. **23,** 370 and 2131. [2] *Ibid.* **23,** 2628 ; **24,** 528.
[3] *Ibid.* **23,** 393. [4] J. prakt. Chem. [2] **23,** 321 ; **34,** 51.

with *i.*-fructose.[1] (2) It was not supposed that the want of carbon dioxide could be supplied to a given plant by formaldehyde until Bokorny[2] recently observed that spirogyra threads in a room free from carbon dioxide grew rapidly in the light at the expense of sodium-oxymethylsulphonic acid, which easily sets free formaldehyde. According to the theory of Baeyer, it seems to me as probable *that plants form pentoses* as that they form hexoses.

I think it is worth the trouble to attempt to find the limit. If pentoses are formed in the leaves of a plant and we find them also in other parts of the plant, it is probable that they have passed to these other parts. The pentosanes so far found form parts of the cell-wall and are soluble in alkalies and in acids only or, in exceptional cases, in boiling water. They correspond to the insoluble hexoses, as cellulose or, perhaps, starch. A migration of this substance as such is not an acceptable explanation, as the pentoses must exist in the plants in an easily soluble form if they really arise by the assimilation-process. In order to prove this I proceeded as follows: 60–80 grams of a finely chopped substance were placed in a 200 cc. wide-neck flask, some drops of chloroform added, the flask filled with distilled water and allowed to stand 12 hours after adding a few more drops of chloroform. The whole mass was then put in a cloth, and the liquid after being pressed out was purified with lead acetate and filtered from the precipitate. It was often necessary to repeat the filtration, as there was further precipitation on standing.

50 cc. of this clear solution was distilled with 50 cc. hydrochloric acid (24 per cent. HCl), and the distillate tested with aniline acetate for furfurol. In this proof I made use of a property possessed by pentoses—that of forming furfurol when heated with hydrochloric acid (12 per cent. HCl).[3] Albuminous bodies which furnish traces of furfurol were not present, but hexoses, which also furnish some furfurol, were always present, and their influence was afterwards shown. Even in solutions which gave much furfurol, the reaction with phloroglucin failed.

I collected the material myself and used the leaves of the following plants in the investigation:

Sonchus asper (Vill.), Compositiae.

Plantago lanceolata (L.), Plantagineae.

[1] Ber. d. chem. Ges. **22**, 359; **23**, 384.   [2] Ber. d. bot. Ges. IX, **4**, 103.   [3] Tollens: *loc. cit.*

Verbascum Thapsus (L.), Scrophulariaceae.
Bignonia capreolata (L.), Bignoniae.
Solanum Carolinense (L.), Solaneae.
Datura Tatula (L.), Solaneae.
Echium vulgare (L.), Bonaginaceae.
Asclepias Cornutii (Decaisne), Asclepiadaceae.
Forsteronia difformis (A. D. C.)?, Apocynaceae.
Diospyros Virginiana (L.), Ebenaceae.
Vaccinium vacillans (Solander), Ericaceae.
Trifolium pratense (L.), Leguminoseae.
Pirus communis (L.), Rosaceae.
Platanus occidentalis (L.), Platanaceae.
Daucus Carota (L.), Umbellifereae.
Euphorbia corollata (L.), Euphorbiaceae.
Vitis cordifolia (Michx), Vitaceae.
Ailanthus glandulosus (Desf.), Simarubaceae.
Hypericum perforatum (L.), Hypericaceae.
Lepidium Virginicum (L.), Crucifereae.
Clematis Ochrolenca (Ait.), Ranunculaceae.
Sassafras officinale (Nees), Lauraceae.
Agrostemna Githago (L.), Caryophyllaceae.
Phytolacca decandra (L.), Phytolaccaceae.
Quercus rubra (L.), Cupulifereae.
Quercus prinus (L.), Cupulifereae.
Quercus lyrata (Walt.), Cupulifereae.
Bromus secalinus (L.), Gramineae.
Carere lupulina (Mühl.), Cyperaceae.
Commelina Virginica (L.), Commelinaceae.
Uvularia perfoliata (L.), Liliaceae.
Pinus Taeda (L.), Conifereae.
Aspidium acrostichoides (Schwartz), Filices.

In the distillates collected furfurol could plainly be distinguished, although the reaction was sometimes very weak. The plants which were used belonged to different families, and I do not think that I am making too broad a statement if I assert that *in the leaves of most of the higher green plants a water-soluble substance occurs which forms furfurol.* I have already remarked that it was possible the furfurol was formed from hexoses. In some cases only traces of furfurol were found, and the amount was never very great. In order to prove that the furfurol which was found was

not formed from the hexoses, it was necessary to estimate (1) how much furfurol the hexoses furnished, and (2) how much furfurol and hexoses were present in the solutions used. In order to solve these questions I have devised a method for determining small amounts of furfurol.

Some time ago Stenhouse[1] obtained a dye-stuff from aniline, aniline hydrochloride and furfurol, of the composition $(C_6H_6N)_2$. $C_5H_4O.HCl.H_2O$.

This dye-stuff is always formed if these substances be used; but if there is enough mineral acid present to combine with all the aniline, no color is produced. Acetic acid, however, acts differently, for a red color immediately appears when aniline and furfurol are added to an alcoholic solution of acetic acid, provided the acid is concentrated enough. The color is very intense, and can be observed in very dilute solutions, and is even formed in very dilute solutions of furfurol in acetic acid, a fact which is made use of for the detection of furfurol in the distillates, where the aniline or aniline acetate neutralises the excess of hydrochloric acid.

I made use of this reaction to determine the furfurol present. 1 cc. of a weak solution of furfurol in 5-per cent. acetic acid was treated in a long tube with 1 cc. of a 1-per cent. solution of aniline in 95-per cent. alcohol. The tube was then sealed up, shaken, and placed in the dark. Another tube containing a solution of furfurol (1 part in 10,000) was prepared in the same way, and the two tubes compared after 20 minutes. If the colors were not the same, the stronger was diluted until they were alike. The amount of furfurol in the solutions used was calculated as follows:

A.—If the solution of unknown strength be the stronger,

$$H = \frac{a+2}{2} \times \frac{1}{10000} \; ; \text{ but}$$

B.—If the standard solution be the stronger,

$$H = \frac{2}{a+2} \times \frac{1}{10000} \; ;$$

where H = value sought, and a = number of cc.'s used. For diluting I always used a mixture of equal parts of the alcoholic aniline solution and of 5-per cent. acetic acid. If I diluted

[1]Ann. Chem. (Liebig) **74**, 282; **156**, 197. Schiff: Ann. Chem. (Liebig) **201**, 355; **239**, 349. De Chalmot: This Journal **14**, 310.

with 50-per cent. alcohol I always added less liquid than the calculated amount, because the aniline acetate formed was somewhat colored, and when a colorless liquid was added this color was diluted too. The acetic acid used was prepared from the sodium salt, for the commercial article often contains traces of furfurol. The alcohol also sometimes contains traces of furfurol which cannot always be removed even by distillation with potassium. To avoid possible mistakes I added a drop of acetic acid to the aniline and allowed it to stand 24 hours before using it, in order to decompose any red coloring matter which was formed at first. This solution had a weak golden-yellow color, which did not interfere with the estimations, if the solutions were diluted as described above. By this method I obtained the following figures:

Calculated.		Found.	
gram furfurol in 1 cc.	cc. necessary to add.[1]	cc. added =	gr. furfurol in 1 cc.
0.001	+ 18	+ 17	0.00095
0.001	+ 18	+ 17.5	0.00097
0.001	+ 18	+ 17.5	0.00097
0.0005	+ 8	+ 8.5	0.000525
0.00004	− 3	− 3	0.00004
0.00004	− 3	− 2.5	0.000044
0.0000167	− 10	− 12	0.000014
0.0000167	− 10	− 9	0.000018
0.0000167	− 10	− 10.5	0.000016

With 0.000008 gram in 1 cc. no color could be detected. The figures found were sufficient for my purpose. In order to determine the amount of furfurol obtained by the distillation with hydrochloric acid, and to obtain some idea of the yield of furfurol from the materials used, I proceeded as follows:

A weighed amount of leaves was chopped up as fine as possible on a tin plate with a knife and transferred to a flask. After adding a few drops of chloroform, 200 cc. of water and a few more drops of chloroform, and allowing the mixture to stand for 12 hours, 20 cc. of lead acetate were added and enough water to make the volume of the liquid 250 cc. This was then well mixed and, after standing half an hour, brought into a strainer and the liquid pressed out and then filtered. 80 cc. of this solution were put in

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[1] The sign + denotes that the unknown solution is the stronger, and − that the standard solution is stronger.

a 100-cc. flask and the excess of lead precipitated with sodium sulphate. The flask was filled up, its contents well mixed and the precipitated lead sulphate filtered off after standing half an hour. 50 cc. of this latter filtrate were distilled with 50 cc. hydrochloric acid (24-per cent. HCl), and the rest used for the determination of the hexoses present (*see below*).

As this solution formed only a small amount of furfurol, only 100 cc. liquid were distilled off. 25 cc. were distilled off slowly with a free flame and then the other 75 cc. more rapidly. 50 cc. of hydrochloric acid (12-per cent. HCl) were added in two portions, the first portion after 25 cc. and the last after 50 cc. had distilled over. The average amount of hydrochloric acid in the distillate was 10 per cent. 16 grams of sodium bicarbonate and 18 grams of sodium acetate were added to this and a solution was obtained, of about 5-per cent. acetic acid and of much sodium chloride and sodium acetate. This was distilled again and the 50 cc. first coming over used in the titration. I afterwards found that the distillate often contained substances which gave a brown color with aniline and interfered with the detection of the red. These substances, however, decompose on standing in the light, while furfurol is not affected, and it was found that without exception the red color could plainly be perceived if the solution was not titrated until the following day.

Even after 24 hours a brown color sometimes remained, and a comparison with a pure furfurol solution was thus not very secure. To test the method the following analyses were made :

1 cc. of 1-per cent. furfurol solution, 100 cc. of 5-per cent. acetic acid, 17 grams sodium chloride and 7 grams sodium acetate were distilled, and 50 cc. were collected.

	Calculated.	Found. I.	II.
Furfurol =	+ 2 cc.	+ 2 cc.	+ (1.5-2) cc.
1 cc. of the solution = 0.0002		0.0002	0.00019 gram

Bignonia capreolata (L.).

I. 80 grams in 250 cc. Furfurol = + 7.5 cc. 1 cc. of the solution = 0.000475 gram of furfurol.

II. 80 grams in 250 cc. Furfurol = + 8 cc. 1 cc. of the solution = 0.0005 gram of furfurol.

I. 80 grams in 250 cc. Furfurol = + 7.5 cc. 1 cc. of the solution = 0.000475 gram of furfurol.

II. 40 grams in 250 cc. Furfurol $= +2.75$ cc. 1 cc. of the solution $= 0.00024$ gram of furfurol. Calculated according to I, it is 0.00024 gram of furfurol.

III. 20 grams in 250 cc. Furfurol $= +0.75$ cc. 1 cc. of the solution $= 0.00014$ gram of furfurol. Calculated according to I, it is 0.00012 gram of furfurol.

Vitis cordifolia (Michx).

I. 80 grams in 250 cc. Furfurol $= -0.75$ cc. 1 cc. of the solution $= 0.000073$ gram of furfurol.

II. 80 grams in 250 cc. Furfurol $= -0.5$ cc. 1 cc. of the solution $= 0.00008$ gram of furfurol.

III. 30 grams in 250 cc. Furfurol $= -10$ cc. 1 cc. of the solution $= 0.000016$ gram of the furfurol. Calculated according to II, it is 0.00003 gram of furfurol.

By this method it was possible for me to answer the question, whether furfurol, which is formed by the distillation of the solution with hydrochloric acid, could or could not be formed from hexoses. I determined the amount of furfurol which soluble hexoses could form, by cane sugar. Commercial granulated sugar was recrystallised from dilute alcohol.

I. 0.1 gram of cane sugar gave traces of furfurol which, however, were only apparent when several cc. were used. By the titration-method no color could be perceived. 1 cc. therefore contained less than 0.000008 gram of furfurol, and 0.1 gram of cane sugar gave less than 0.0004 gram of furfurol.

II. 0.1 gram of cane sugar gave traces of furfurol and no color by titration. Contained less than 0.0004 gram of furfurol.

III. 0.5 gram of cane sugar; slight color visible. 1 cc. contained between 0.00002 and 0.000008 gram of furfurol, or 0.5 gram of cane sugar formed 0.001–0.0004 gram of furfurol.

IV. 0.5 gram cane sugar; result same as III.

Therefore 1 gram of invert sugar ($= 0.95$ gram cane sugar) gave, at the most, 0.0019 gram of furfurol, or about 0.2 per cent.

I now took some of the leaves which, in my opinion, yielded the smallest amount of furfurol and estimated in the solution the furfurol and hexoses. I could make only an approximate determination of the largest amount of hexoses possible. 40 cc. of the clear solution (see above) were treated successively with lead acetate and with sodium sulphate, and after being subjected to the

process of inversion and neutralised, were filled up to 50 cc. The traces of dissolved chloroform, which would even reduce copper, were removed by inversion.

Fehling's solution was titrated with the liquid thus obtained. I titrated only 2 cc. of the Fehling's solution (1 cc. of blue and 1 cc. of white), which I diluted to 50 cc. The value of the Fehling's solution[1] was estimated by 0.25-per cent. invert sugar solution made according to Soxhlet:[2]

2 cc. of the Fehling's solution was reduced by 4.5 cc. of this solution and was equivalent to 0.01125 gram of invert sugar.

Trifolium pratense (L.).

Used 70 grams; 2 cc. Fehling's solution $=$ 7 cc. of the solution; furfurol $= +$ 2.5 cc.

1 gram substance $=$ 0.0089 gram of invert sugar.[3]

1 gram substance $=$ 0.001 gram of furfurol.

The amount of hexoses present in 1 gram of the substance could have furnished, at the most, 0.0000178 gram of furfurol.

Solanum Carolinense (L.).

Used 70 grams; 2 cc. Fehling's solution $=$ 18.2 cc. of the solution; furfurol $= -$ (1.5–2) cc.

1 gram substance $=$ 0.0035 gram of invert sugar.

1 gram substance $=$ 0.00023 gram of furfurol.

The hexoses could have formed, at the most, 0.000007 gram of furfurol.

Verbascum Thapsus (L.).

Used 80 grams; 2 cc. Fehling's solution $=$ 4 cc. of the solution; furfurol $= -$ 8.5 cc.

1 gram substance $=$ 0.0136 gram of invert sugar.

1 gram substance $=$ 0.000084 gram of furfurol.

The hexoses could have formed, at the most, 0.000027 gram of furfurol.

Trachelospermum difforme (Gray ?).

Used 80 grams; 2 cc. Fehling's solution $=$ 3 cc. of the solution; furfurol $= -$ 3 cc.

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[1] The copper sulphate used was somewhat weathered.

[2] J. prakt. Chem. [2] **21**, 228.

[3] These figures are too high, as I took no account of the solid matter and air in the solution; but the figures for the furfurol and invert sugar are subject to the same errors.

1 gram of the substance $=$ 0.0183 gram of invert sugar.

1 gram of the substance $=$ 0.00016 gram of furfurol.

The hexoses could have formed, at the most, 0.000037 gram of furfurol.

Daucus Carota (L.).

Used 80 grams; 2 cc. Fehling's solution $=$ 3 cc. of the solution; furfurol $= -1.5$ cc.

1 gram of the substance $=$ 0.0183 gram of invert sugar.

1 gram of the substance $=$ 0.00022 gram of furfurol.

The hexoses could have formed, at the most, 0.000037 gram of furfurol.

From the figures obtained it appears that in all the cases examined the amount of hexoses was not sufficient to explain the formation of furfurol.

As I have already stated, the five plants used in this investigation are those which in my opinion were shown, in the first investigation, to yield the smallest amount of furfurol, and with the exception of *Trifolium*, this suggestion seems to be true.

I extend my previous conclusion and now express it as follows:

In most (all) of the higher green plants there are soluble substances in the leaves which form furfurol, and are neither albuminous substances nor hexoses, but must be regarded in the present state of our knowledge as pentoses.

The amount of soluble pentoses in the leaves is very small and much less than that of the hexoses.

While I considered that these soluble pentoses furnish 50 per cent. of the furfurol, I calculated the following approximate figures:

	Hexose.	Pentose.
Bignonia	...	0.37 per cent.
Trifolium	0.89 per cent.	0.20
Solanum	0.35	0.45
Daucus	1.80	0.45
Trachelospermum	1.80	0.03
Verbascum	1.40	0.008

The investigations described were carried on with leaves, and it is possible that a soluble pentose might be present in these which was absent in the rest of the plant and therefore did not serve as a carrier of the pentose. For this reason I examined the bark also, and in this investigation used only the colorless bark of young limbs.

Ailanthus glandulosus (Desf.).

Used 80 grams; furfurol $= -1.5$ cc.; 1 gram substance $=$ 0.00022 gram of furfurol.

Sassafras officinale (Nees).

Used 80 grams; 2 cc. Fehling's solution$= 2.5$ cc. of the solution; furfurol $= -(1.5-2)$ cc. 1 gram substance $= 0.022$ gram of invert sugar; 1 gram substance $= 0.00021$ gram of furfurol. The hexoses could have formed, at the most, 0.000044 gram of furfurol.

Quercus rubra (L.).[1]

Used 80 grams; 2 cc. Fehling's solution $= 5.5$ cc. of the solution; furfurol $= -0.5$ cc. 1 gram substance $= 0.01$ gram of invert sugar; 1 gram of substance $= 0.00031$ gram of furfurol. The hexoses could have formed, at the most, 0.00002 gram of furfurol.

According to this, *soluble pentoses occur in the colorless bark of higher green plants*. If the soluble pentoses found were transportable substances, it seems to me likely that they would easily diffuse through membranes permeable to water. It was shown that large quantities of the substances in the sap of the *Phytolacca* which form furfurol, could diffuse through parchment paper in 36 hours.

Further experiments were conducted as follows:

Datura Tatula (L.).

200 cc. of the pressed-out sap were treated successively with lead acetate and with sodium sulphate, and the clear liquid placed in a . dialyser of parchment with distilled water outside. The analysis of the liquid outside, after 6 hours, was as follows: 2 cc. of Fehling's solution $= 7.5$ cc. of the solution (in which the process of inversion had taken place; furfurol $= -(1.5-2)$ cc. 1 cc. $=$ 0.0019 gram of invert sugar; 1 cc. $= 0.000053$ gram of furfurol. The hexoses could have formed, at the most, only 0.0000038 gram of furfurol.

Phytolacca decandra (L.).

The conditions were the same in this case as in the last, and the results were as follows:

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[1] Part of the young wood was still adhering to the bark.

2 cc. of Fehling's solution $=$ 17 cc. of the solution (also changed by inversion); furfurol $= -$1.5 cc.   1 cc. $=$ 0.0008 gram of invert sugar;   1 cc. $=$ 0.000057 gram of furfurol.   The hexoses could have formed, at the most, 0.0000016 gram of furfurol.

By this it is proved that *the soluble pentoses are easily diffusible.* The question arises now, whether we shall regard them as simple sugars or as more complex substances.   The solubility and diffusibility point towards the former.   Moreover, the complex pentoses generally have an acid character, so, had soluble salts been present, they would probably have been precipitated by the lead acetate.   I think, therefore, *that there are present in plants simple pentoses which serve as transporting substances.*   Absolute proof of this could be obtained if the sugar could be isolated; and this seems to be not at all impossible—for instance, from the leaves of the *Bignonia*, in which I calculated there was about 0.4 per cent. Most of the hexoses can be easily separated from a solution by fermentation; but I could not carry out this line of investigation, as my laboratory was not fitted up for such work.   It seemed probable that *the small amount of soluble pentoses would be scarcely diminished upon the death of the leaves,* if these substances were only migratory substances; and such proved to be the case, as the plants used lost their leaves about the beginning of September from a drought.

Pirus communis (L.).

From this tree I collected equal numbers of green and of yellow leaves of the same size.   The yellow leaves were about to fall.

I. August 26.

Yellow.	Green.
112 leaves weighing 26 grams:	112 leaves weighing 31 grams:
Furfurol$= -$0. cc.	Furfurol$= -$(0.5-1.) cc.

The aniline reaction of the yellow leaves upon the addition of 0.5 cc. was the same as that of the green.   The proportion of soluble pentoses in the yellow leaves to those in the green was about as 5 : 4.

II. August 29.   (The same tree.)

Yellow.	Green.
128 leaves weighing 27.5 grams:	128 leaves weighing 32.5 grams:
Furfurol$= \pm$0. cc.	Furfurol$= -$0.5 cc.

The aniline reaction and the proportion were the same here as in the last case.

Bignonia capreolata (L.).

Yellow and green leaves of the same size were used.

Yellow.	Green.
500 leaves weighing 60.5 grams:	500 leaves weighing 70.5 grams:
Furfurol $= +3.5$ cc.	Furfurol $= +5.$ cc.

0.5 cc. had to be added to the green leaves in order to make the two agree by the aniline reaction. The proportion of soluble pentoses in yellow and green leaves was as $4:5$.

If by the assimilation-process pentoses are formed, it is probable that they cannot pass out of the leaves as fast as they are formed. The hexoses, as is well known, are deposited as starch. I shall return to the question whether or not pentoses too are deposited temporarily as solid matter. I shall now point out that most probably there are more soluble pentoses in the leaves in the evening than in the morning, assuming that the theory of their formation by assimilation is correct.

If the pentoses are temporarily precipitated after their formation by the assimilation-process, then, presumably, they migrate after the principal assimilation is over. If the pentoses accumulate only in solution, the difference between the various parts of the plants might be equalised by the next morning. In the first case the difference in the amount of soluble pentoses in the leaves in the morning and in the evening would be less striking than in the latter. I thought it would repay one to examine this.

An investigation was first carried on with *Bignonia capreolata*, which contains a large amount of soluble pentoses. I collected the samples carefully and made four determinations of each, but found no great difference between the leaves collected in the morning and those in the afternoon. *Platanus* gave no results, although three experiments were made with material from different stations. *Quercus* gave different results, which I shall give here.

Quercus Lyrata (Walt.).

1. Damp ground. Leaves from a small tree which had a southern exposure. A sunny day.

August 11, 8.30 P. M.; 30 leaves $= 535 \times 305.5$ cm.; 2 leaves $= 31 \times 17$; $32 = 566 \times 325.5$ cm. Furfurol $= -(3-4)$ cc.

August 12, 4.30 A. M.; 30 leaves $= 564 \times 321.5$ cm.$= 48.5$ grams. Furfurol $= -11$ cc.

The reaction was much stronger in the evening, than in the morning leaves.

2. Same place and conditions.

August 19, 7 P. M.; 50 leaves $= 702 \times 393.5$ cm.$= 43.5$ grams. Furfurol $= -1$ cc.

August 19, 4.30 A. M.; 50 leaves $= 703.5 \times 393$ cm.$= 43.5$ grams. Furfurol $= -(1.5-2)$ cc.

The leaves collected in the evening were 0.5–1 cc. stronger than those gathered in the morning.

3. Damp ground, southern exposure. Specimen was taken from a tree. The day was slightly cloudy.

August 22, 9 P. M.; 46 leaves $= 629 \times 277.5$ cm.$= 34$ grams. Furfurol $= -2.5$ cc.

August 22, 4.30 A. M.; 46 leaves $= 651.5 \times 243.5$ cm.$= 39.5$ grams. Furfurol $= -1$ cc.

The leaves in the evening were 0.5–1 cc. weaker than in the morning.

4. Same plant as those used in 3. Dark day.

August 24, 8.30 P.M.; 45 leaves $= 620 \times 318$ cm.$= 35.5$ grams. Furfurol $= -2$ cc.

August 24, 4.30 A. M.; 45 leaves $= 619 \times 314$ cm.$= 35.5$ grams. Furfurol $= -(2.5-3.)$ cc.

Leaves gathered in evening were 0.5 cc. stronger than those gathered in morning.

5. In the valley. A bush. A partly cloudy day.

August 29, 8 P. M.; 30 leaves $= 513 \times 248.5$ cm.$= 37.5$ grams. Furfurol $= -1$ cc.

August 30, 4 A. M.; 30 leaves $= 513.5 \times 248$ cm.$= 36.5$ grams. Furfurol $= -1.5$ cc.

Leaves gathered in the evening were 0–0.5 cc. stronger than those gathered in the morning ; this difference is quite perceptible.

6. Large tree near the bush used in 5 ; all the leaves from the same branch.

August 29, 8 P. M.; 49 leaves $= 651 \times 379$ cm.$= 45$ grams. Furfurol $= -(0.0-0.5)$ cc.

August 30, 4 A. M.; 49 leaves $= 649 \times 381.5$ cm.$= 45$ grams. Furfurol $= -1$ cc.

Leaves gathered in evening were 0.5 cc. stronger than those gathered in the morning.

Quercus prinus (L.).

7. A tree on a southern exposure. Sunny day.

August 15, 8.30 P. M.; 45 leaves 661.5 × 313 cm. = 51.5 grams. Furfurol = ± 0 cc.

August 15, 4.30 A. M.; 45 leaves = 664 × 314 cm. = 57 grams. Furfurol = —2 cc.

Leaves gathered in the evening were 1.5–2 cc. stronger than those gathered in the morning.

8. August 16, 7.30 P. M.; 45 leaves = 668 × 314 cm. = 48 grams. Furfurol = —1 cc.

August 16, 5 A. M.; 45 leaves = 657 × 313.5 cm. = 49.5 grams. Furfurol = —2.5 cc.

Leaves gathered in the evening were 0.5–1 cc. stronger than those gathered in the morning.

Quercus rubra (L.).

9. August 24, 8 P. M.; 25 leaves = 450 × 280 cm. = 49.5 grams. Furfurol = —(2–2.5) cc.

August 24, 5.30 A. M.; 25 leaves = 451 × 279 cm. = 48 grams. Furfurol = —2 cc.

Leaves gathered in the morning same as those gathered in the evening.

In comparing these results one cannot help concluding that they agree very closely, especially when he recognises that the methods of research were not very exact, and that the samples were collected altogether in the woods, which makes it quite difficult to obtain accurate samples.

In these experiments in seven cases there was unquestionably an excess of soluble pentoses in the leaves gathered in the evening over that in those gathered in the morning. In one case (*Quercus rubra*) the amount was about the same in both sets of leaves. In experiment 3, the leaves gathered in the morning were richer; but in experiment 4, the leaves of the same plant were used and the result was reversed.

I would be justified in concluding from this that *in the leaves of* Quercus (lyrata *and* prinus) *there are more soluble pentoses present in the evening than in the morning.* I carried out no investigations with other plants, the difficulty of gathering samples in the woods being considerable, especially at night; nevertheless I hope to repeat these experiments and to extend them. I was not surprised that species of oak acted as described, since the wood of the nearly related beech contains a very large amount of

pentosanes. I did not obtain any positive knowledge as to the amount of pentosanes in oak wood, but I found that C. Koch had extracted 10 per cent. of gum from it and that this probably contained only a small part of the pentosanes present.

I return now to the hypothesis which was mentioned above: *Pentoses which arise by assimilation-processes should, like the hexoses, be precipitated in changing to an insoluble form.* If pentoses and hexoses are formed at the same time, it would be necessary for me to accept this hypothesis. I suppose it would be necessary, in order that the assimilation might be continuous, that the parts assimilated should be removed or precipitated to give an opportunity for continued action. It might not be possible for the plants to convey them away as fast as they are formed, in which case they would be precipitated. One must assume a temporary precipitation of the pentoses in the chlorophyl grains mixed with the hexoses as parts of the starch of assimilation. Unfortunately there is no means available at present for identifying a pentose under the microscope, although it may soon be possible. The presence in plants of pentosanes which act very much like starch is very probable, since Winterstein[1] obtained 15 per cent. of furfurol from the amyloid materials of the poconia and balsam seeds.

Although there are more soluble pentoses in the oak leaves in the evening than in the morning, still the difference is only slight. It was impossible for me to detect any difference using *Bignonia* and *Platanus* leaves. It does not seem to me possible that the excess of the soluble pentoses found in the oak makes up the whole or any considerable part of the pentoses assimilated daily. It is very probable that the principal migration of the pentoses stored up during the daytime commences at sunset, just as this is believed of the hexoses. I have carried on experiments to determine whether or not a difference in the amount of pentoses in the leaves in the morning and at night can be proved. In the leaves of the trees which were most suitable for the purpose I found about 10 per cent. of the dry substance was pentosanes. If only a small part of this be carried away during the night it would be very difficult to detect it, and very exact methods would have to be used to determine it. The experiments which have been carried on later suggest that more pentosane is present in the evening, but the results are not sufficient even for a pre-

[1] See ref. 1.

liminary statement. I hope to continue this work next summer and carry the investigations further. Let it be understood, however, that I am not inclined to regard the hypothesis offered as entirely true, for I fear I have gone too far in my attempts to find an analogy with the hexoses ; but if the hypothesis is proved, it and the results communicated above will safely establish the origin of pentoses by assimilation. I must finally return to my former proposition that the substance assimilated should be withdrawn from further action in order that there may be continued assimilation.

I do not propose to suggest any new hypothesis ; on the contrary I think it highly probable that this has already been pointed out, but I do not know that such is the case. It will, however, do no harm to make some remarks on the subject.

Although in the plants other carbohydrates than pentoses are present, perhaps nonose (Fischer) and others, yet the greater part of the dried material consists of hexoses and hexosanes. The starch formed by assimilation behaves micro-chemically like that formed in other ways, and probably consists of hexosanes. The conception that plants form chiefly hexoses by assimilation is still universal.

By the same reactions one can make heptose artificially from hexose, octose from heptose, etc., just as well as hexose from pentose. If plants really form hexoses by condensation from simpler aldehydes, there is no apparent reason why the condensation should not go further and why larger amounts of heptoses, octoses, nonoses, etc., should not be formed. Fischer[1] thinks that plants form hexoses and, perhaps, nonoses from glyceric aldehyde, but the nonoses have not been isolated, as their behavior is very similar to that of the glucoses. This is, however, only a supposition which does not explain the formation of pentoses. Under the conditions in which a condensation of $x\,CH_2O$ to $(CH_2O)_x$ takes place in the plants, the reverse might also be possible; we ought then to express the equivalent reaction thus :

$$x\,(CH_2O)_n \rightleftarrows (CH_2O)_{x\,\times\,n}.$$
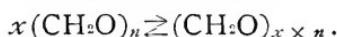
This seems possible especially as there is here simple condensation only, without any closing of rings. The compounds $x\,CH_2O$ in which $x < 5$, ought then to be present, but they have not yet been isolated from the higher plants. By the

[1] Ber. d. chem. Ges. **23,** 2238.

artificial condensation of formic aldehyde a mixture of compounds in different stages of the condensation was actually obtained. If the substances formed in some special stage of the reaction are removed or precipitated, the preceding statements become clear.

Résumé.

There are generally present in plants substances (pentosanes) which form pentoses.

All the natural pentoses so far known belong to the *l.*-series, and all the natural hexoses to the *d.*-series. Plants by assimilation either form hexoses and pentoses, or have the power to change *d.*- into *l.*-compounds. The theory of Baeyer, which has lately received fresh support, makes it not improbable that both hexoses and pentoses are formed. The present work was undertaken to determine the limits of the reactions. Soluble pentoses which could be identified as wandering substances were sought.

It was possible in all the cases which were examined to show the presence of soluble substances which form furfurol; but these substances might be hexoses which furnish traces of furfurol. On this account it was necessary to estimate how much furfurol the hexoses which were present could form and how much furfurol was formed.

For the estimation of small amounts of furfurol a method was devised which depended on the color-reaction between furfurol and aniline in acetic-acid solution.

By this method it was proved that the amount of hexoses present was not at all sufficient to explain the formation of all the furfurol, and that therefore soluble pentoses were present.

For these experiments leaves and colorless bark were used. The amount of soluble pentoses is much less than that of soluble hexoses.

The soluble pentoses are easily diffusible through membranes. The facts lead to the conclusion that the soluble pentoses are simple sugars, $C_5H_{10}O_5$. The investigation confirmed the belief that the small amount of soluble pentoses is not perceptibly diminished by the death of the leaves. In the leaves of the oak there was found in the evening a small but evident excess in the amount of soluble pentoses over that found in the morning. Joined to this is the hypothesis that the pentoses are temporarily converted into stable forms directly after their formation by the assimilation-process. This hypothesis will be further discussed.

METAMIDOPHENOL AND ITS DERIVATIVES.

First Paper.

By M. Ikuta.

By the reduction of metanitrophenol (melting-point, 96°) with tin and hydrochloric acid, Bantlin[1] obtained a hydrochloride of a base crystallising in colorless grains, which is stable only in the dry state. On account of its instability, the free base could not be isolated. The same salt seems to have been obtained later by Pfaff[2] as a reduction-product of monobrommetanitrophenol of the melting-point 110°. The free metamidophenol being considered to be very unstable, only few of its derivatives,—namely, the methyl[3] and ethyl[4] ethers—have been obtained from the corresponding ethers of metanitrophenol by reduction.

Since the discovery of excellent dyestuffs of the rhodamine group[5] in 1887, metamidophenol and its alkyl derivatives have attained such an importance in the color industry that a number of new methods[6] for producing the same have been patented. According to these patents, metamidophenol is a crystalline body remarkably stable in the air. As the latter methods afford us a ready means of obtaining the substance, it seemed desirable to investigate and characterise it from a scientific side, and to confirm the one or the other statement, which are in themselves widely different.

The result of my work, which will be continued and extended to mono- and dialkyl derivatives, confirms the latter statement— namely, that metamidophenol is a remarkably stable and crystalline body, forming a number of well defined derivatives.

Metamidophenol, $C_6H_4{<}^{OH\ (1)}_{NH_2\ (3)}$.—The substance is made according to the method of A. Leonhardt & Co.,[7] which not only

[1] Ber. d. chem. Ges. **11**, 2101.   [2] *Ibid.* **16**, 613.

[3] Pfaff: *Ibid.* **16**, 614, 1139.   [4] Wagner: J. prakt. Chem. [2], **32**, 73.

[5] D. R. P. (German patent) 44002, Badische Anilin und Soda Fabrik.

[6] D. R. P. 44792, Bad. A. & S. F.; D. R. P. 48151, Bad. A. & S. F.; D. R. P. 49060, A. Leonhardt & Co.

[7] D. R. P. 49060.

gives a fair yield, but is simple in operation and best adapted for laboratory preparation:

A mixture of 10 grams resorcin, 6 grams ammonium chloride and 20 grams ammonia (10-per cent.), is heated in a sealed tube at 200° for ten hours. The resulting pale-yellow solution is acidified with a large excess of hydrochloric or sulphuric acid, and extracted with ether to free it from unchanged resorcin. On neutralising with soda, part of the metamidophenol separates out in greenish-gray crystals. Ether extracts the rest of the substance from the mother-liquor. It is best purified by dissolving the crude product in toluene, in which the coloring impurities are not soluble, while the substance crystallises out almost immediately in colorless prisms, having a constant melting-point of 122°–123°. D. R. P. 44792 gives the melting-point as 121° and D. R. P. 49060 as 120°. About 50 per cent. of the theoretical yield is thus obtained pure.

For the analysis, it was recrystallised from benzene and dried at 100°.

0.1511 gram substance gave 0.3650 gram CO_2 and 0.0924 gram H_2O.

0.2001 gram substance gave 24.2 cc. N at 30° and 751 mm.

	Theory for C_6H_7NO.	Found.
C	66.05	65.88
H	6.42	6.79
N	12.84	12.96

The substance is easily soluble in alcohol, ether, glacial acetic acid, and water; less soluble in toluene and benzene; and practically insoluble in chloroform, carbon bisulphide and petroleum ether. It is freely soluble in acids and alkalies, forming crystalline salts with the former.

Its alkaline solution is not stable in the air, and even its aqueous solution is very sensitive towards all oxidising agents, including ferric chloride, which gives a brownish-yellow color.

With benzoquinone, it forms a dark-violet body, crystallising in scales.

Metamidophenol, when pure and dry, can be kept without change.

Salts of metamidophenol.—Hydrochloric, hydrobromic, hydriodic and sulphuric acids form with metamidophenol very stable

and crystalline salts. These are extremely soluble in water, but are not deliquescent; they are more or less easily soluble in boiling absolute alcohol. They can be sublimed with partial decomposition. The aqueous solutions are strongly acid towards litmus.

All the salts described below were made by adding a calculated quantity of metamidophenol to the respective acids (1 molecule) and evaporating on a water-bath until crystals begin to appear on the surface. While the solution was slowly cooling in a desiccator, most of the salt separated out in large transparent crystals. After drying on clay plates, it was again recrystallised from water.

The hydrochloride, C_6H_7NO. HCl, crystallises in colorless prisms from water and melts at 229°.

0.2014 gram substance, dried at 110°, gave 0.1983 gram AgCl.

	Theory for $C_6H_7NO.HCl$.	Found.
Cl	24.39	24.35

The hydrobromide, $C_6H_7NO.HBr$, crystallises in colorless prisms and melts at 224°.

0.1995 gram substance, dried at 110°, gave 0.1963 gram AgBr.

	Theory for $C_6H_7NO.HBr$.	Found.
Br	42.11	41.87

The hydriodide, $C_6H_7NO.HI$, crystallises in similar prisms and melts at 209°.

0.2001 gram substance, dried at 110°, gave 0.1982 gram AgI.

	Theory for $C_6H_7NO.HI$.	Found.
I	53.48	53.43

The acid sulphate, $C_6H_7NO.H_2SO_4$, crystallises in colorless, rectangular tablets or in needles, and melts at 152°.

0.2056 gram substance, dried at 105°, gave 0.2341 gram BaSO₄.

	Theory for $C_6H_7NO.H_2SO_4$.	Found.
H_2SO_4	47.34	47.87

Monacetylmetamidophenol (metoxyacetanilide),

$C_6H_4{\displaystyle <}^{OH}_{N=C_2H_4O.}$ —1 gram metamidophenol mixed with 1.1 grams acetic anhydride warms up immediately to form a clear solution. In a few minutes the whole thing solidifies to a crystalline mass, consisting of fine needles. After digesting with a little water and filtering, the product is practically pure. It may be

further purified by recrystallisation from water and is thus obtained in colorless needles, melting at 148° to 149°.

0.1540 gram substance, dried at 105°, gave 0.3574 gram CO_2 and 0.0859 gram H_2O.

0.1979 gram substance, dried at 105°, gave 17 cc. N at 30° and 753 mm.

	Theory for $C_8H_9NO_2$.	Found.
C	63.57	63.29
H	5.96	6.19
N	9.27	9.23

It is easily soluble in alcohol and in water, and difficultly soluble in benzene, ether, and chloroform. On account of its greater solubility in water than in ether, the presence of a free hydroxyl group is recognised by using a cold saturated solution containing undissolved substance, which is immediately dissolved on adding a few drops of sodic hydrate.

It gives no isocyanide reaction with chloroform and alcoholic potash, and forms a benzoyl derivative by means of Baumann-Schotten's reaction.

Diacetylmetamidophenol, $C_6H_4{<}{\substack{O.C_2H_3O \\ N=C_2H_4O}}$.—1 gram metamidophenol is mixed with 3 to 4 grams of acetic anhydride. In order to complete the reaction, the mixture is heated up to about 150° to 160° for from two to three hours. The product is digested with absolute alcohol and evaporated on a water-bath. The thick oily residue is then taken up with ether, and the latter is repeatedly washed with dilute sodic hydrate and sulphuric acid. After drying the ethereal solution with calcium chloride and evaporating off the ether, 1.5 grams of colorless oil are left behind. The oil will solidify on standing for several hours. It is purified by dissolving in benzene to which a little petroleum ether is added afterwards. Diacetylmetamidophenol will crystallise out in colorless scales, melting constant at 101°.

0.2014 gram substance, dried at 75°, gave 0.4575 gram CO_2 and 0.1103 gram H_2O.

0.1659 gram substance, dried at 75°, gave 11 cc. N at 27° and 750 mm.

	Theory for $C_{10}H_{11}NO_3$.	Found.
C	62.17	61.95
H	5.69	6.08
N	7.25	7.22

The substance is easily soluble in alcohol and ether, less so in benzene and water, and but very slightly soluble in petroleum ether. Its solution in water is unaffected by ferric chloride.

Dilute acids and alkalies do not extract the substance from its ethereal solution.

Monobenzoylmetamidophenol (metoxybenzanilide),

$C_6H_4{<}^{OH}_{N=C_7H_6O}$.—1 gram of the dibenzoylmetamidophenol described below is dissolved in absolute alcohol and to the solution the theoretical amount of alcoholic potash (2 molecules) is added. The mixture is kept boiling on a water-bath for about two hours. Potassium benzoate will separate out in colorless scales ; this is filtered off and the filtrate is evaporated to dryness. The residue is dissolved in about 10 cc. of water containing a little sodic hydrate. Dilute acid will then precipitate the substance in the form of a white powder. After crystallising twice from toluene, it is obtained in colorless silky needles melting at 174°.

0.1479 gram substance, dried at 125°, gave 0.3967 gram CO_2 and 0.0722 gram H_2O.

0.2281 gram substance, dried at 125°, gave 13.7 cc. N at 30° and 751 mm.

	Theory for $C_{13}H_{11}NO_2$.	Found.
C	73.24	73.15
H	5.16	5.42
N	6.57	6.44

The substance is very easily soluble in alcohol and in ether ; less so in toluene and in chloroform, and sparingly soluble in benzene and water. Sodic hydrate dissolves the substance without change.

The isomeric benzoyl derivative $NH_2.C_6H_4.O.C_7H_5O$ could not be obtained from the dibenzoyl body by saponification with either acid or alkali.

Dibenzoylmetamidophenol, $C_6H_4{<}^{O.C_7H_5O}_{N=C_7H_6O}$. — 1.5 grams metamidophenol, dissolved in 15 grams sodic hydrate (10-per cent.), and 4 grams benzoyl chloride are gradually mixed together with brisk shaking. A thick oil is at first formed, but it solidifies to a hard crust on standing. The crude product is powdered in a mortar and washed thoroughly with a fresh quantity of sodic

hydrate. On crystallising twice from benzene, the substance is obtained in minute bundles of prismatic crystals. It can be recrystallised from absolute alcohol, from which it separates out in colorless scales. The melting-point is 153°.

0.2041 gram substance, dried at 125°, gave 0.5660 gram CO_2 and 0.0978 gram H_2O.

0.2479 gram substance, dried at 125°, gave 10.5 cc. N at 27° and 748 mm.

	Theory for $C_{20}H_{15}NO_3$.	Found.
C	75.71	75 63
H	4.73	5.32
N	4.42	4.59

It is moderately soluble in alcohol and in chloroform; less so in benzene; sparingly soluble in ether, and insoluble in water and in petroleum ether. The substance is insoluble in dilute acids and alkalies.

Tribrommetamidophenol, $C_6HBr_3\!<^{OH}_{NH_2}$.—1 gram metamido-phenol, dissolved in glacial acetic acid (95-per cent.), is treated with 4.5 grams of bromine. The latter is readily absorbed with a separation of a white precipitate, hydrobromic acid being at the same time evolved. Water is then added, when a large quantity of bulky white needles is thrown down. After drying on a clay plate, the product is purified by dissolving it in petroleum ether, (boiling-point 70°–80°), from which it crystallises out in bright long needles melting at 121°.

0.2319 gram substance, dried at 100°, gave 8 cc. N at 22° and 763 mm.

0.1582 gram substance, dried at 100°, gave 0.2560 gram AgBr (Carius).

	Theory for $C_6H_4Br_3NO$.	Found.
N	4.04	3.92
Br	69.36	68.52

Tribrommetamidophenol is easily soluble in alcohol and in acetic acid; less so in petroleum ether, and slightly soluble in boiling water with decomposition.

It is freely soluble in dilute alkalies, but on account of its negative groups, the substance is no longer soluble in acids.

WORCESTER, MASS., *August,* 1892.

THE SOLUBILITY OF TRIPHENYLMETHANE IN BENZENE.

By C. E. Linebarger.

There is undoubtedly an intimate relation between the surface energy of crystals and their power of entering into solution. The "solution-tensions" of the various forms in which the same chemical substance can crystallise are different; their solubilities accordingly differ, for saturated solutions are cases of dynamical equilibrium, *i. e.* the velocity with which molecules detach themselves from the solid to enter into solution becomes equal to the velocity with which molecules are precipitated from solution upon the solid. The nearer study of the crystalline forms of compounds, especially organic, shows that they are numerous and varied. Triphenylmethane, for instance, exhibits a great variety of crystals, which have been studied by Nölting.[1] It was my intention in beginning this investigation to determine the solubility of some of the polymorphic forms described by him. I found, however, that their solubilities are so nearly identical and the labile modifications pass so easily into the stable, that it was impossible to obtain results that might be counted as reliable for all forms. In this paper there are given only the solubility of the molecular compound of triphenylmethane and benzene, $(C_6H_5)_3CH + C_6H_6$, and that of the stablest form of triphenylmethane (obtained by slow crystallisation from alcohol) in benzene.

The determinations were made as follows: The solid compound in large excess was for two to three hours shaken up frequently with benzene in a flask set in a thermostat, the temperature of which did not vary more than 0.1° during the determination. A portion of the solution was then pipetted off into a small long-necked flask and, after weighing, the benzene distilled off by means of a free flame. To remove the last traces of benzene from the residual triphenylmethane, the flask was set in an air-bath kept at a temperature of 200°. About 20 grams of solution were taken for each determination, and duplicates did not vary more than one or two figures in the second decimal place. The results are given in Table I and represented graphically in Fig. 1.

[1] Ztschr. Kryst. **5**, 472.

TABLE I.

Tempera-tures.	Pts. $(C_6H_5)_3CH$ to 100 pts. C_6H_6.	Tempera-tures.	Pts. $(C_6H_5)_3CH$ to 100 pts. C_6H_6.	Tempera-tures.	Pts. $(C_6H_5)_3CH$ to 100 pts. C_6H_6.
3.9°	3.90	19.4°	7.24	50.1°	30.64
4	4.06	23.1	8.95	55.5	40.51
12.5	5.18	37.5	10.48	71.	140.00
13	5.51	42.	19.61	76.2	319.67
16.1	6.83	44.6	22.64		

FIG. 1.
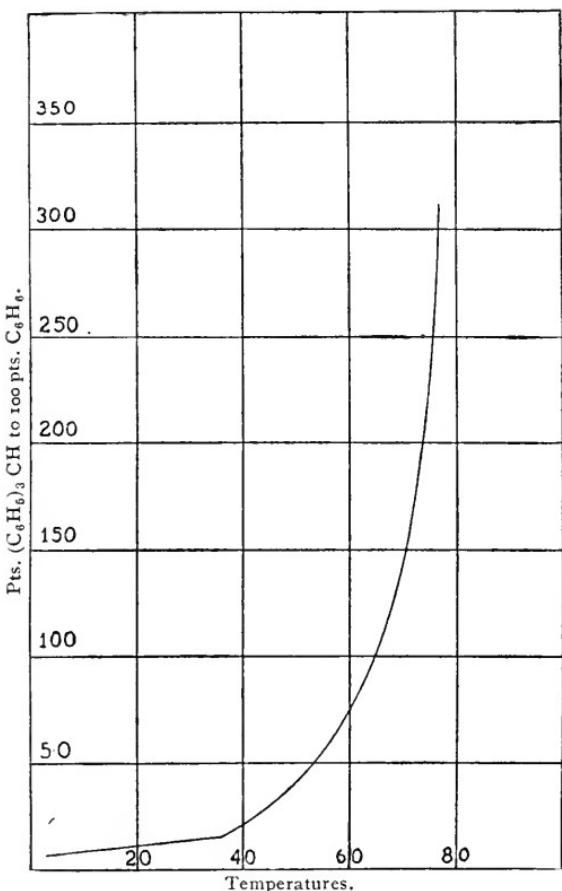
If a solution of triphenylmethane in benzene be cooled slowly, supersaturation being prevented by the addition of crystals of triphenylmethane and benzene, the molecular compound of the two hydrocarbons, $(C_6H_5)_3CH + C_6H_6$, crystallises out until the temperature 3.9° is reached. At this point crystals of benzene begin to form also. The curve of solubility here meets the curve

which expresses the dependence of the freezing-point of the solution upon its concentration. As the benzene freezes, the concentration of the solution becomes greater and a corresponding quantity of the double compound, $(C_6H_5)_3CH + C_6H_6$, separates out. A mechanical mixture of crystallised benzene and the double compound, $(C_6H_5)_3CH + C_6H_6$, in proportions corresponding to the concentration of the saturated solution is accordingly obtained. As such a solution does not become changed through partial solidification, it follows that it must have a constant freezing-point, or, what amounts to the same thing, the solid mixture must have a fixed melting-point. That the above mixture is not a chemical compound, as is stated for similar cases by certain scientists, the above considerations amply show.

The solubility of the triphenylmethane at its "cryohydratic point" is so slight that the solution may truly be termed dilute, and the laws which have been established concerning dilute solutions are entirely applicable in this case. Thus it has been shown that the lowering of the freezing-point (Δt) of the solvent brought about by the presence of a dissolved substance with a molecular mass equal to M may be found by means of the equation

$$\Delta t = E \frac{m}{M},$$

where m represents the percentage composition of the solution and E the molecular depression of the freezing-point. At 3.9°, the freezing-point of the solution, it was ascertained that 100 parts of benzene dissolve 3.90 parts of triphenylmethane. Substituting these values in the above equation, we find $\Delta t = 0.799°$. The benzene employed melted at 4.73°, which is 0.83° higher than the point of fusion of the cryohydrate. This agrees within the limits of the unavoidable experimental errors with the value for Δt obtained by calculation.

Quite a general view is obtained of the states of equilibrium of the system, benzene and triphenylmethane, by a consideration of their solubilities. At 3.9° four phases are coexistent: 1. benzene (solid); 2. molecular compound of triphenylmethane and benzene (solid); 3. solution of triphenylmethane in benzene (liquid); 4. mixture of the vapors of benzene and triphenylmethane.

We have accordingly $n + 2$ phases of n chemical compounds and the temperature 3.9° marks a quadruple point of transition.

With rise of temperature phase 1., *i. e.* benzene (solid), disappears, and the system consists of but $n + 1$ phases until the temperature 37.5° is reached. Here the curve of solubilities changes abruptly. The curve up to this point has been almost a straight line but slightly inclined towards the axis of abscissæ. Now, however, it commences to rise more and more rapidly. This change in the direction of the curve indicates that some change must take place at 37.5°. As a matter of fact, this is the point at which the molecular compound of triphenylmethane and benzene decomposes into its constituent molecules. Above 37.5° the molecular compound is in labile, below that temperature in stable equilibrium. I have been unable to obtain solutions saturated with the molecular compound above 37.5°, so easily is it decomposed. Triphenylmethane does not, however, combine immediately and completely with benzene when introduced into it and kept at a temperature a little below 37.5°. Thus I have been able to obtain solutions of triphenylmethane at 35°–36°. At 37.5° a new phase comes into existence, *viz.* triphenylmethane (solid), and this temperature is another quadruple point of transition. The $n + 2$ coexistent phases are: 1. molecular compound of triphenylmethane and benzene (solid); 2. triphenylmethane (solid); 3. solution of triphenylmethane in benzene (liquid); 4. mixture of the vapors of triphenylmethane and benzene (gaseous).

Above 37.5° the solubility increases very rapidly until a temperature of 76.2° is reached, which is the melting-point of the molecular compound in closed tube. At this temperature the quantities of triphenylmethane and benzene are in molecular proportions, and solid trimethylmethane disappears. As the temperature now rises, benzene passes off rapidly as vapor, for its boiling-point is but 4° above this last point of transition. At 94.3°, the melting-point of pure triphenylmethane, the system loses benzene entirely and is reduced to a single chemical compound. 94.3° is accordingly a triple point of transition.

The system above studied is an excellent instance of the way in which the acts of solution and of melting pass continuously into each other. At 3.9° the cryohydrate melts; solution ensues, the solid being the molecular compound of triphenylmethane and benzene; at 37.5° this decomposes into its constituent hydrocarbons; at 76.2° complete fusion takes place, etc.

When benzene is added slowly to finely powdered triphenyl-

methane it is absorbed with evolution of heat. If the resulting dry mass be heated, it changes into a more or less viscous liquid at a certain temperature. If the benzene and triphenylmethane be mixed in molecular proportions, this occurs at 76°, the melting-point of the compound $CH(C_6H_5)_3 + C_6H_6$. If more benzene be added, however, liquidity takes place at lower temperatures. A homogeneous solution is not in reality obtained, but rather a suspension of the triphenylmethane in its solution. The temperature at which liquefaction takes place may be determined within a degree or so, as follows: The mixture, contained in a small Erlenmeyer flask, is heated in a glycerine-bath until it becomes liquid. The bath is then allowed to cool and the flask tilted so as to cause some of the solution to run upon the sides. On bringing the flask to a vertical position, so long as the mass is liquid it quickly runs down, while, if at all solidified, it does not move. By repeating this procedure several times the true temperature of solidification is obtained. In Table II are given the results of some determinations.

Table II.

Temperature.	$CH(C_6H_5)_3$ in grams.	C_6H_6 in grams.	Molecules of C_6H_6 to 1 mol. $CH(C_6H_5)_3$.	Solubility pts. $CH(C_6H_5)_3$ to 100 pts. benzene.
52°	4.88	5.50	3.52	36.92
45	4.88	6.37	4.08	23.04
17	4.88	8.29	5.31	6.98

An inspection of the table shows that the temperatures are functions of the solubilities. The explanation of the phenomena is obvious. For every temperature there is a minimum quantity of triphenylmethane which can be so disseminated throughout the solution that it deprives the latter in a measure of its mobility. As the solubility increases the temperature rises, the point at which liquefaction occurs rises also, since more of the solid triphenylmethane passes into the dissolved (liquid) state.

CHICAGO, *December* 19, 1892.

REVIEWS AND REPORTS.

At the meeting of the International Chemical Congress, held in Paris in the summer of 1889, a special Section was appointed to consider the unification of chemical nomenclature, and, after discussing a variety of propositions, some of which were adopted, it was decided to form an International Commission for the further study of the subject.[2]

The members resident in Paris, having been constituted a permanent committee of the Commission, have devoted an immense amount of time and care to the preparation of a scheme, and it was to discuss their report[3] that we met at Geneva on Easter Monday last. The French Committee had issued invitations, not only to members of the Commission, but also to many other prominent chemists, so that the meeting was a thoroughly representative one. It is worth mentioning, as an illustration of the sympathetic treatment accorded by public bodies in France to men of science, that the Paris-Lyons-Marseilles Railway Company granted a reduction of one-half of the fare over their line to members of the Congress.

Very happily, the local committee had arranged that all might stay at the one hotel—the Métropole—and it was here that we first met in friendly union on the Monday evening.[4] The next

[2] The following chemists eventually consented to serve on the Commission: Messrs. Béhal, Berthelot, Bouveault, Combes, Fanconnier, Friedel, Gautier, Grimaux, Jungfleish, Schutzenberger (all representing France), Graebe (Switzerland), Alexejeff and Beilstein (Russia), von Baeyer and Nolting (Germany), Lieben (Austria), Paterno (Italy), Franchimont (Holland), Armstrong (England), Istrati (Roumania), Calderon (Spain), Cleve (Sweden), Boukowski Bey (Turkey), Ira Remsen (United States), and Mourgues (Chili).
[3] This report had been prepared by the following: Messrs. Friedel (President), Béhal, Bouveault, Combes, Fanconnier, Gautier, and Grimaux.
[4] The following is the official list of those who took part in the Conference: Messrs. H. E. Armstrong, Professor at the Central Institution, London, Secretary of the Chemical Society; A. Arnaud, Professor at the Museum, Paris; Adolphe von Baeyer, Professor at the University of Munich; Barbier, Professor at the Faculty of Sciences of Lyons; Aug. Béhal, Professor at the Superior School of Pharmacy of Paris; Louis Bouveault, Doctor of Science, Paris; Stanislas Canizzaro, Professor at the University of Rome; Paul Cazeneuve, Professor of the Faculty of Medicine of Lyons; Alphonse Combes, Doctor of Science, Paris; Alphonse Cosso, Director of the Experimental Station of Agriculture, at Turin; Maurice de Lacre, Professor at the University of Gand; Michel Fileti, Professor at the University of Turin; Emil Fischer, Professor at the University of Würzburg; A. P. N. Franchimont, Professor at the University of Leyden; Charles Friedel, Member of the Institute, Professor at the Sorbonne, Paris; Dr. J. H. Gladstone, F. R. S., London; Carl Graebe, Professor of the University of Geneva; Phillippe-Auguste Guye, Professor at the University of Geneva; Istrati, Professor at the University of Bucharest; Albert Haller, Professor of the Faculty of Science of Nancy; Maurice Hanriot, Fellow-Professor of the Faculty of Medicine, Paris; A. R. Hantsch, Professor at the Polytechnic School of Zurich; Achille Le Bel, Doctor of Science, Paris; A. Lieben, Professor of the University of Vienna; Leon Maquenne, Doctor of Science, Assistant Naturalist at the Museum, Paris; von Meyer, Professor at the University of Leipsic; Denis Monnier, Professor of the University of Geneva; R. Nietzki, Professor of the University of Bale; Emilio Noelting, Director of the School of Chemistry of Mulhouse; Emmanuel Paterno, Professor at the University of Palermo; Amé Pictet, Instructor at the University of Geneva; William Ramsay, F. R. S., Professor of the University of London; Zdenko-H. Skraup, Professor of the University of Graz; Ferdinand Tiemann, Professor of the University of Berlin.
  The Local Committee was composed of the following: Messrs. Emile Ador, H. W. de Blonay, Alex. Claparede, Prof. C. Graebe, Prof. Ph. A. Guye, Alex. Le Royer, Prof. Denis Monnier, Amé Pictet, Fred. Reverdin, Prof. Albert Rilliet, Edouard Sarasin.

morning the Congress assembled at the Hotel de Ville, M. Richard, the Cantonal Minister of Education, being in the chair. After an admirable address of welcome from this gentleman, who appeared to thoroughly appreciate the importance of the object in view, on the motion of Prof. Canizzaro it was wisely decided not to follow the complimentary, but somewhat unbusinesslike Continental practice so frequently adopted, of appointing a different chairman each day, but to have only one. M. Friedel, who had taken the chair at all the numerous meetings of the Paris Committee, having been chosen by acclamation President of the Conference, formal business was at once entered into, and, after the necessary interval for lunch, the sitting was resumed in the afternoon. We met in like manner on the two following days, and the final sitting took place on the Friday morning, but many had left before this. On Tuesday evening, by invitation of the local committee, we visited the theatre, a very beautiful building. On the Wednesday evening we were entertained by them at a dinner at the Hotel Métropole, on which occasion a very striking speech was delivered by Prof. von Baeyer, who, after pointing out that experimental chemistry had been carried, early in the century, into Germany from France by Liebig, who was tutored by Gay-Lussac, proceeded to say that, although the science had now undoubtedly reached its highest development in Germany, it was more than probable that, in the future, circumstances would arise which would lead to some other nation—France, Russia, Italy, or England—coming to the fore. On this occasion, on the motion of M. Le Bel, it was unanimously decided to appoint M. Marignac Honorary President of the Congress, and a letter to him expressing our regret that ill-health prevented his taking part in its work was at once signed by all present. We were indebted in many other ways to the local committee, and there is no doubt that the success of the meeting was in large measure due to the forethought and hospitable care exercised by them on our behalf. Absolute amity prevailed throughout, and it was clear that all were bent on co-operating to secure the carrying out to a successful issue of a very difficult but most important work. The great advantage to be derived from the personal intercourse which such meetings promote was soon apparent ; gradually, the doubts which many entertained as to the possibility of devising a practical, rational scheme of nomenclature were dispersed, and ere many hours had elapsed the sympathies of all present were enlisted on behalf of the work ; thus a mission has been sent forth which will explain the enterprise to chemists generally.

The resolutions passed at the meetings are appended to this article. These, I think, are in no way to be taken as in all respects final, but they will serve to prepare the way and to indicate the lines on which the work is to be carried out. The position in which we found ourselves placed, in fact, was not one which justified our arriving at decisions which could fairly be regarded as

binding.   The report of the French Committee was placed in our hands only on the morning of the first meeting, and it was impossible to master its contents at so short a notice, and still less to criticise and test the application of its recommendations in detail. That the scheme would serve but as the basis for discussion was soon evident, when at the very outset a system of nomenclature for the hydrocarbons was adopted very different and far more significant than that recommended in the report ; and numerous other departures from its recommendations were carried in the course of the proceedings.   Again, some of the most active members of the Congress had confessedly paid attention only to special groups of compounds, and had not tested the application of proposals which they strenuously advocated to compounds of other groups ; but as a nomenclature admirably adapted to one class may be open to all sorts of objections when applied to another, the general bearing of recommendations made with reference to special groups will have to be fully considered before they can be finally adopted.   The resolutions relating to fatty acids (Nos. 18, 19) are of this kind, and their adoption was warmly opposed by an important minority on the ground that, however well they might be adapted to acids pure and simple derived from open-chain hydrocarbons, their application to acids derived from closed-chain hydrocarbons and acids containing other radicles in addition to carboxyl was beset with difficulty.   In order to name an acid in accordance with this resolution, the formula of the corresponding hydrocarbon must be constructed from that of the acid by changing carboxyl into methyl; for example, citric acid, $CH_2(CO_2H).C(OH)(COOH).CH_2(COOH)$, would have to be regarded as a derivative of methylpentane, and would be named methylpentanoltrioic acid, numerals being adding to indicate the positions of the hydroxyl and carboxyl groups ; in like manner, mellitic acid, $C_6(COOH)_6$, would be named hexamethyl-benzenehexoic acid, although no methyl is present in it. The mental effort involved in visualising the formulæ from such names as these would appear to be far greater than if they were respectively named propanoltricarboxylic acid and benzenehexacarboxylic acid, or simply propanoltri-acid and benzenehex-acid, the use of the term *acid* being understood to imply the presence of carboxyl.   A decision on points such as these can only be arrived at after careful study of the general effect of such a proposal, and there was no time for such a comparison during the brief debate possible at a Conference.   In some cases, there can be no doubt that the full force of objections raised to proposals in favor of which a majority subsequently voted was not felt, owing to the difficulty which necessarily arises at an international Conference if the language used be not equally familiar to all present, and consequently full expression cannot be given by all to their views.   Moreover, although it is easy to criticise destructively even at short notice, constructive criticism under such circumstances is very difficult; consequently a proposal may be accepted even in face of serious

objections to its adoption simply because nothing better can be suggested at the time. An instructive case of the kind arose on discussing thio-compounds. The proposals in French report were not regarded as altogether satisfactory, and an amendment was suggested and carried which to many appeared most undesirable; the next morning, when the time came to confirm the resolutions arrived at on the previous day, the discussion was reopened, and a slight modification of the original proposal was suggested, which was recognised to be an improvement, and the objectionable resolution was rescinded. Clearly at such meetings much must depend on the right expression being found by happy inspiration at the right moment.

The one resolution which covers all others, and which defines the nature of the task to be undertaken, is the first. Whatever name we may choose to apply to a substance colloquially, it is clearly an absolute necessity of the times that every compound should bear a *systematic* name, of such a character that it can be at once translated into the corresponding formula; and that, *vice versa*, a name corresponding to any particular formula may be devised which we may count on finding in the *official* register, if the compound thought of have been described. The value of such a systematic nomenclature to original workers as well as to students cannot be overestimated, and few who are qualified to take part in such a work will grudge the time they may spend on it. There was considerable difference of opinion at the meeting as to whether a systematic nomenclature should be devised merely for the purpose of an official register, or whether the object aimed at should be a system of wider application; the majority, I believe, came to the conclusion that it should certainly subserve the one, but if possible both purposes. There can be little doubt, however, that the future student will cut the knot by declining to burden his memory with a double vocabulary in the case of all but the commonest substances, and that therefore there is but one course open to us (cf. Res. 26).

Although sufficiently conservative to retain methane, ethane, propane and butane, the Congress decided not to adopt the proposal to continue the use of the names formic, acetic, propionic, and butyric for the first four acids of the acetic series, which was advocated by a substantial minority, on the ground that their retention would facilitate the change from the old to the proposed new system. This is one of the questions demanding careful consideration. Many will, no doubt, prefer to retain old unsystematic names as far as possible, but it is easy to see that the desire to avoid change may carry us too far in this direction; it will undoubtedly be very inconvenient to the present generation of chemists to abandon familiar and cherished names, but nevertheless it may be a wise course to boldly face the difficulty, rather than inflict on coming generations a partially illogical and unsystematic nomenclature. The argument that the present familiar names

may still be used colloquially is, as I have already said, scarcely a justification of the dismissal of such names from the official nomenclature, as our successors may be expected to object more and more decidedly to a multiplex system as chemical science progresses, and to insist on the adoption of the official as the sole system ; the extent to which familiar trivial names shall be retained in the official system is therefore a matter of great importance.

As one aim and object must be to devise a system which is significant and logical throughout, no considerations must be allowed to prevail which will defeat this, and it will not suffice to quote present usage in support of illogical proposals; but this has been done. Thus the Congress decided (Res. 46) to name compounds of the type $R'.N_2.R'$ *azo*-compounds, while retaining the name *diazo*-chloride for $C_6H_5.N_2Cl$. It matters not to us that the manufacturers have chosen to call the colors derived from *diazo*-compounds azo-dyes; if substances such as $(C_6H_5)_2S$ are termed *thio*, and compounds such as $(C_6H_5)_2S_2$ *di*-thio compounds (Res. 43), we are bound to be consistent, and apply the significant term diazo to substances containing two nitrogen atoms. Resolution 46 ought therefore to be in part rescinded. I call attention to this case as an illustration of the tendency to break away from uniformity in favor of what may fairly be termed popular prejudice, which will require to be most carefully guarded against if the various sections of our system are to harmonise.

It will be gratifying to English chemists that the principle advocated for many years past by our Chemical Society, and enforced in its " Instructions to Abstractors "—that particular terminations should be regarded as indicative of particular functions, and should therefore be restricted to particular classes of compounds—has been legalised and extended by the Congress. This is a step of great importance, as we may expect that it will affect even trivial names, and that in future names will be given to new substances which will to a certain extent afford a clue to their nature ; the hopeless confusion which now reigns supreme in the pages of the *Berichte*, for example, owing to the disregard of this principle by our German colleagues—who have hitherto been, as a rule, almost uniformly neglectful in matters of nomenclature—will, it may be hoped, ere long give way to more orderly treatment.

But the importance of applying this principle logically was not fully grasped even at the Congress, inasmuch as it was decided to affix the termination *ine* to acetylenic hydrocarbons, notwithstanding that this termination is admittedly indicative of basic properties. If, however, a suitable suffix ending in *ene* could be thought of, there would probably be little difficulty in securing its acceptance, in which case unsaturated hydrocarbons generally would have names ending in *ene*, and saturated hydrocarbons names ending in *ane*, and these terminations could be reserved exclusively for hydrocarbons.

It will be obvious from the foregoing remarks that although a

solid foundation for our future system of nomenclature has been laid, much remains to be done before a mature design, perfect in all its details, can be presented for adoption. At the meeting the hope was expressed that a decision might be speedily taken to enable Beilstein to utilise the proposals in the preparation of the third edition of his marvelous work; but it is clear that we are not yet so far advanced as to make this possible or even desirable, and it would be most unfortunate if Beilstein were at the present juncture to promulgate a system which is manifestly incomplete; nothing can be worse in such a case than to consent in haste, when it is evident that this would surely involve repentance at leisure.

Those of us who are interested in the work, and competent to advance it, must now test in detail the application of the proposals which have been provisionally adopted, and we must assist in contributing to the ultimate establishment of a system on the broad lines of policy laid down for our guidance at the Congress. As it is not improbable that in the future, owing to the extended use of our language, the major proportion of chemical students will speak English, it is essential that due attention be paid to the matter here in England, so that a system may be devised which we can make use of without difficulty.

Resolutions taken by the Congress.

1. In addition to the usual methods of nomenclature, an *official* name, permitting of distinguishing each body under a distinctive title, will be established. The Congress requests authors to mention in their articles the official name in parenthesis, in addition to the name chosen by them.

2. It is decided to consider, for the present only, those bodies of a known constitution, leaving for later consideration bodies of unknown constitution.

3. The termination *ane* is adopted for all the saturated hydrocarbons of the fatty series.

4. The old names of the first four saturated hydrocarbons (*methane, ethane, propane, butane*) are retained; the names derived from the Greek numbers will be used for those which have more than four atoms of carbon. These names will distinguish the normal hydrocarbons.

5. The hydrocarbons with an open chain are regarded as derivatives of the normal hydrocarbons, and their name will be derived from the longest normal chain that can be established in their formula.

6. The numbering of the lateral chains will be drawn from the atom of terminal carbon nearest in a lateral chain; in the case where the lateral chains nearest to the extremities will be placed symmetrically, the simplest will decide the choice.

7. Whenever a residue is substituted in a lateral chain, *metho-*, *etho-*, are employed instead of *methyl-*, *ethyl-*, prefixes reserved for the case where the substitution takes place in the principal chain.

8. In the hydrocarbons having only one *double bond*, the termination *ane* of the corresponding saturated hydrocarbon will be replaced by the termination *ene* (ex. ethene) ; in those having two *double bonds*, the termination *diene* will be used (ex. propadiene) ; those having three, *triene*, etc. If it is necessary, the place of the double bond is indicated by the number of the first atom of carbon to which this double bond is attached.

9. The names of the hydrocarbons with a *triple bond* will be terminated in like manner with *ine, diine, triine* (ex. ethine for acetylene, propine for allylene, hexadiine for dipropargyle).

10. In the case where occur simultaneously both *double* and triple bonds, the terminations *enine, dienine*, etc., will be employed.

11. The saturated hydrocarbons with a closed chain will take the names of the corresponding saturated hydrocarbons of the fatty series preceded by the prefix *cyclo* (ex. cyclohexane for hexamethylene).

12. The atoms of carbon in a lateral chain will be distinguished by the same number as the atom of carbon to which the chain is attached. They will carry a number which will indicate their distance from the point of attachment in the lateral chain.

In the case where two chains are attached to the same atom of carbon, the numbers of the most simple among them will be accented.

The same method of numbering is adopted for the lateral chains of the closed chains.

13. The non-saturated hydrocarbons will be numbered as the corresponding saturated hydrocarbons. In case of doubt or the absence of a lateral chain, the number 1 will be placed before the terminal carbon the nearest to the bond highest in order.

14. The numbering of the hydrocarbons is retained for all their substitution products.

15. The alcohols and the phenols will be called after the name of the hydrocarbon from which they are derived, terminated with the suffix *ol* (ex. pentanol, pentenol, etc.).

16. Concerning the polyatomic alcohols and phenols, one of the particles *di, tri, tetra*, etc., following the order of the polyatomicity, will be inserted between the name of the fundamental hydrocarbon and the suffix *ol* (ex. propane-triol for glycerin).

17. The name of *mercaptan* is abandoned, and this function will be distinguished by the suffix *thiol* (ex. ethane-thiol).

18. In the acids of the fatty series, the carboxyl will be considered as forming an integral part of the carbon skeleton.

19. The name of all the monobasic acids of the fatty series is derived from that of the corresponding hydrocarbon followed by the suffix *oic*.

The polybasic acids will be distinguished by the terminations *dioic, trioic, tetroic*, etc.

20. For the monovalent residues of the acids, the *oic* of the acid will be changed to *oyle*.

21. In the monobasic acids with the symmetrical or saturated normal chain, the carbon of the carboxyl bears the number 1.

22. The acids in which one or several atoms of sulphur replace as many atoms of oxygen of the carboxyl will be distinguished as follows: The sulfur simply united with an atom of carbon will be designated by the suffix *thiol;* if the bond is double, the suffix *thion* will be used.   Examples:

> $CH_3.CO.SH.$ Acid-ethane-thiolic.
> $CH_3.CS.OH.$ Acid-ethane-thionic.
> $CH_3.CS.SH.$ Acid-ethane-thionthiolic.

23. The Congress gives its adhesion to the following proposition, without expressing a definite vote on the subject:

The oxy-ethers will be designated by the names of the hydrocarbons which compose them, united by the term *oxy-* (ex. pentane-oxy-ethane for ethyl or amyl oxide).

24. The anhydrides of the acids will retain their present mode of designation after the name of their acids (ex. anhydride ethanoic).

25. (12 *bis.*) In the case of two lateral chains attached to the same atom of carbon, the order in which these are expressed will correspond to their degree of complication.

26. A more exhaustive discussion of the bodies with complex functions is postponed, and the study of this question is referred to the International Commission, in order that it may prepare upon this point a plan which will be laid before the next Congress. The Commission will endeavor to reconcile the exigencies of the spoken nomenclature with that of a terminology applicable to the dictionaries.

27. The customary methods for the salts or compound ethers are retained.

28. The lactones will be designated by the word *olide*, indicating that it is an internal anhydride of alcohol and acid. The position of the alcoholic function, as to the carboxyl of the acid alcohol whence proceeds the lactone, can be expressed by the Greek letters a, β, γ, δ, in addition to the usual numbering of the lateral chains:

$$O \underline{\quad\quad} CO$$
$$CH_3-CH-CH_2-CH_2$$

1.4 pentanolide or 1.4 γ pentanolide.
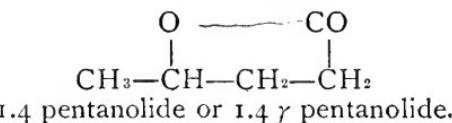
29. The lactonic acids derived from bibasic acids will be named after the lactones from which they are derived, adding the suffix *oic*, characteristic of the acids.

30. The discussion of the closed chains is postponed until the publication of the ideas of Mr. Armstrong upon this subject, will permit the International Commission to compare them with the propositions of Mr. Bouveault.

31. In the aromatic series and all the bodies containing a closed chain, all the lateral chains will be considered as substituting.

32. Aldehydes will be distinguished by the suffix *al* (methanal, ethanal).

Sulfo aldehydes : suffix *thial.*

33. Acetones : suffix *one* ($CH_3.CO.CH_2.CH_3$, butanone 2).

Diacetones, triacetones : suffixes *dione, trione.*

Sulfoacetones : suffix *thione.*

34. Quinones : The suffix *quinone* for the bodies homologous to ordinary quinone.

The bodies having the chain CO.CO several times will be di-quinones or triquinones.

35. Ammoniacal compounds : no change (ex. ethylamine, ethene-diamine).

The bodies where the bivalent group—NH—closes a chain formed of positive radicles will be called *imines* (ex. ethene-imine).

Phosphines, arsines, stibines, sulphines : the nomenclature in use is retained.

Hydroxylamine : this name is retained.

36. Hydroxylamine : this name is retained.

37. Oximes : will be designated by following the rules at present admitted : the *isonitroso* bodies will be called oximes.

<div style="text-align:center">

(Ex. $CH(NOH).CH_2.CH_2CH_3$ 1 Butanoxione.

$CH_3.CH_2C(NOH).CH_3$ 2 Butanoxime.)

</div>

38. Amides : this name is retained (ex. ethanamide.

<div style="text-align:center">

$NH_2.CO.CH_2.CH_2.CO.NH_2$ Butanes diamide.

$COOH.CO.CH_2.CH_2.CO.NH_2$ Butanamidoic acid).

</div>

Imides : will be retained.

Amidoximes : this name will be retained.

<div style="text-align:center">

(Ex. $CH_3.C(NOH).NH_2$ Ethanamidoxime.)

</div>

Urea : the generic word *urea* will be retained, and will be employed as a suffix for the alcoholic derivatives of urea, while the derivatives from an acid substitution will be called *ureides.*

The bodies containing two molecules of urea will be distinguished by the suffixes *diurea, diureide.* The acid ureides will take the name *ureic acids.* The terminations *uramic* and *uric* are abandoned.

39. Amidines : this suffix will be retained.

<div style="text-align:center">

(Ex. $CH_3.C.NH.NH_2$ Ethanamidine.)

</div>

For the derivatives the name will be doubled, and the name of the substituting group will be preceded by, either amino, or amidine, as the case may be.

<div style="text-align:center">

(Ex. $CH_3.C(NC_2H_5).NH_2$ Ethanamino ethylimidine.

$CH_3.C(NH).NHC_2H_5$ Ethanethylamino-imidine.)

</div>

Guanidines : the generic word *guaniaine* is retained, but different guanidines will be named as substitution derivatives of diamido-carbo-imidine.

40. Betaines : suffix *taïne.*

<div style="text-align:center">

(Ex. $N(CH_3)_3$—O   Ethanoyltrimethyltaine).

CH_2————CO

</div>

41. Nitriles: the question is left in suspension for the fatty series. The prefix *cyano* (as a name of the substituting body) is adopted for the aromatic series.

42. Carbylamines: the nomenclature in use is retained.

43. Sulfones: this name is retained.

(Ex. $C_6H_5.SO_2.C_6H_5$ Benzene-sulfone-benzene).

Sulphides: will be designated by putting *thio* between the two saturated components (provisionary decision).

(Ex. $C_6H_5.S.C_6H_5$ Benzene-thio-benzene).

Disulfides: will be designated in the same manner by *dithio*.

44. Isocyanic ethers: suffix *carbonimid*. Ex. The ethyl cyanate of Wurtz will be called ethylcarbonimid. The corresponding sulfo-derivative will be called in the same manner ethylthiocarbonimid.

Cyanates: this name is retained for the true ethers which, by saponification, give cyanic acid or its direct product of hydration. The name sulfocyanate will be replaced by *thiocyanate.*

45. Nitro bodies: the nomenclature in use is not changed.

46. Azo bodies: the terms *azo* and *diazo* are retained, but the mode of enunciating these compositions will be modified as follows:

(Ex. $C_6H_5.N_2.Cl$ Diazobenzene chloride.
$C_6H_5.N_2.C_6H_5$ Benzene-azo-benzene.
$C_6H_5.N_2.C_6H_4.N_2.C_6H_5$ Benzene-azo-benzene-azo-benzene).

HENRY E. ARMSTRONG.

THE MAGNETIC ROTATION OF COMPOUNDS SUPPOSED TO CONTAIN ACETYL, OR TO BE OF KETONIC ORIGIN.

A few years ago a review of some work by W. H. Perkin on the relation between chemical composition and magnetic rotation appeared in this Journal.[1] Since then Mr. Perkin has been engaged principally in studying the effect of variation of chemical constitution on magnetic rotation, and in a paper which has just been published[2] he submits the evidence obtained by the application of this physical method to the determination of the structure of that much investigated compound, ethyl acetoacetate. The principal results are given below.

No definite relationship between chemical composition and magnetic rotation was discovered until 1882, as the method of calculating the experimental results consisted in comparing the magnetic rotatory effect of unit lengths of liquids. Mr. Perkin says: "If unit lengths of vapor could be examined, some useful information might be obtained, because these lengths would contain the same number of molecules." On account of the experimental difficulties of determining the rotation produced by gases, he examined the magnetic rotation per unit length of liquids,

[1] This Journal 6, 356.   [2] J. Chem. Soc. 61, 800-864.

and attained the same end by referring the results of the observations to the lengths of columns of liquid which would be formed by the condensation of unit lengths of vapor. The lengths compared were thus directly proportional to the molecular weights and inversely proportional to the densities of the two liquids, and the ratio of the rotations produced by such lengths of the substance under examination and of the standard substance when placed in the same magnetic field, is called the *molecular magnetic rotation.* The quantity thus defined was found to depend not only upon the composition of the molecule but also upon its constitution.

The effect of composition is illustrated in any series of similarly constituted compounds. A constant difference in composition of successive members corresponds to a constant difference in their molecular magnetic rotation. Thus, in the series of normal hydrocarbons, to the constant difference in composition CH_2, corresponds the constant difference in molecular magnetic rotation 1.023. Moreover, a difference in composition of CH_2 produces this same difference of molecular rotation in the other homologous series. In general, a number can be found for every homologous series which, when increased by 1.023 times the number of carbon atoms in a given member of the series, will give its molecular rotation. This number is called the *series-constant* and varies with the constitution, being different even for the series of primary and secondary alcohols. For the series of normal hydrocarbons the series-constant is 0.513. To obtain the rotation of hexane we add to this 6×1.023, and the sum, 6.651, agrees very well with the molecular rotation actually observed, 6.646.

In determining the chemical constitution of a compound, its chemical behavior will usually limit the number of possible formulæ which might be applied to it. Thus, in the case of ethyl acetoacetate, only two formulæ can be considered:

$$(1)\ CH_3.CO.CH_2.COOC_2H_5,\ \text{and}$$
$$(2)\ CH_3.C(OH) = CH.COOC_2H_5.$$

Both agree more or less closely with its chemical conduct. According to one of these formulæ, the compound is unsaturated; according to the other, it is plainly a saturated ketone.

The molecular rotatory power of saturated compounds is, however, much smaller than that of the corresponding unsaturated compounds. By a determination of the molecular rotation of ethyl acetoacetate it should therefore be possible to determine which of the two formulæ above is the correct one.

This was done some years ago, and the value obtained agreed very well with that calculated on the basis of formula 1. Accordingly formula 1 was adopted, and now Perkin examines the rotation of a large number of other acetyl derivatives, in some of which there can hardly be any other than a ketonic structure, to test the validity of his conclusion.

Among the substances examined were the following :

Pyruvic acid, $CH_3.CO.COOH$.—This substance could hardly have any other than the above structure. The molecular rotation observed agreed with that calculated on this assumption.

Ethyl acetoacetate.—The molecular rotation was examined at 16° and at 90°, and was found to agree approximately with that calculated on the basis of the ketonic formula. At the higher temperature the rotation is somewhat less and indicates, if anything, that any small amount of the unsaturated isomer which might be present at the lower temperature is decreased ; so that at higher temperatures the substance would probably act more like a ketone and less like an unsaturated compound than at lower temperatures.

Ethyl ethylacetoacetate, $CH_3CO.CH.C_2H_5.COOC_2H_5$. — This substance was examined so that a comparison could be made with ethyl ethylmalonate, in which case there is no possibility of a hydroxy structure. The difference between the molecular rotations of ethyl ethylacetoacetate and ethyl acetoacetate was the same as the difference between those of ethyl ethylmalonate and ethyl malonate, indicating that the replacement of ethyl is analogous in both cases. In ethyl ethylmalonate it is directly in combination with carbon.

Ethyl allylacetoacetate, $CH_3.CO.CH.COOC_2H_5$. — This was

$$CH_2.CH:CH_2$$

examined on account of its unsaturated condition, and the molecular rotation indicated the presence of only one double bond in the compound.

Levulinic acid, *β-Acetopropionic acid*.—The molecular rotation agreed with the ketonic formula, $CH_3.CO.CH_2.CH_2.COOH$. The acid was examined because it was thought that it might be more capable than the ethereal salts of changing to the hydroxy form, $CH_3.C(OH):CH.CH_2.COOH$.

Ethyl acetonedicarboxylate.—This is ethyl acetoacetate with a hydrogen atom of the acetyl group replaced by a negative group, *viz.* $COOC_2H_5$. The rotation observed was found to be slightly high at ordinary temperatures, indicating the presence of some of the hydroxylic isomer. On re-examination at 94°, the rotation agreed very well with that calculated from the ketonic formula. Perkin thinks that at ordinary temperatures some of the hydroxy isomer is present, due to the influence of the negative group $COOC_2H_5$.

Diketonic compounds.—A number of these were examined. Besides a monohydroxy isomer there is here also the possibility of a dihydroxy isomer. Thus acetylacetone might have any one of the following structures :

(1) $CH_3.CO.CH_2.CO.CH_3$,
(2) $CH_3.C(OH):CH.CO.CH_3$,
(3) $CH_3.C(OH):C:C(OH).CH_3$.

The interest attached to the examination of this compound arises from the fact that the molecular rotation observed at ordinary temperatures was very large, indicating it to be a hydroxy unsaturated compound with about 20 per cent. of the isomeric dihydroxylic compound. At 93° the rotation corresponded to that of a mixture of the diketonic and hydroxyketonic compounds. When cooled it quickly regained its original rotation.

The methyl derivative showed a much weaker tendency to pass over into its hydroxylic isomers, and the ethyl derivative showed this tendency in a still smaller degree. The methyl derivative passed readily into the diketonic modification on heating to 90°, but retained its constitution for some time after it had cooled, as was shown both by its molecular rotation and its density.

The examination of the molecular refraction and dispersion, which also enables us to distinguish between saturated and unsaturated compounds, led to similar conclusions, and it may be said here that, wherever both the magnetic rotation and refraction and dispersion of a compound have been examined, the results obtained by the one method are in strict accordance with those obtained by the other.

Triketonic compounds.— The only one examined, diacetyl-acetone, was found at 60° to consist of the dihydroxylic isomer. The constitution also changes with the temperature.

The existence of products consisting of two or more isomeric compounds side by side, their relative proportions varying with the temperature, is remarkable and may have, as Mr. Perkin says, something to do with the way these products behave in different reactions.

He intends to examine mixtures of some of these compounds with different reagents, as this might show whether the relative proportions of the isomers present are dependent on the reagent used. The results of such an investigation will be awaited with much interest. F. A. Wolff, Jr.

A List of the More Important Changes in the Spelling and Pronunciation of Chemical Terms, recommended by the American Association for the Advancement of Science, with the Reasons Therefor.

Elements.—*Aluminum* is spelled in the shortened form in deference to the wishes of technical chemists, on account of the growing importance of the metal in manufactures.

Cesium loses the *a* of the diphthong, as unnecessary, while the new form is in harmony with the French and Italian orthography.

Columbium replaces *Niobium* as a matter of historical justice. It was called columbium by its discoverer.

Glucinum is preferred to *Beryllium* on the same ground of historical priority.

Sulfur is modified in accordance with the general phonetic simplification going on in our language. The new form brings us into accord with the French, German and Italian usage. The replacement of **ph** by **f** is carried out in all the derivatives. (It has not been deemed advisable to yield at present to the wish of many, that a similar change should be made in the spelling of phosphorus, as the German and French languages still retain the **ph**.)

The termination **-ic.**—This is used for metals only when there is a contrast with **-ous**, thereby avoiding several non-euphonious terms, and bringing us into accord with the British custom. Thus avoid aluminic, zincic, strontic, etc.

The termination **-ol.**—This is used exclusively for alcohols, and and all alcohols receive the termination. This also is in harmony with British usage, and brings about a most desirable simplification and uniformity. Thus, glycerol, quinol, etc.

Terminations in **-id.**—The final **e** is dropped from all chemical terms formerly ending in **-ide**, and the pronunciation is always -ĭd.[1] Of the three pronunciations of this termination— -îde, -ĭde, and -īde—in varying degrees of use amongst us, the second appeared undoubtedly the most preferable for the following reasons: -îde is an uncommon, almost unnatural pronunciation of the vowel in our language, although it would bring us into unison with European usage and simplify phonetic values for the ears of foreigners; -īde leads frequently to confusion with -īte (sulfīde and sulfīte) and is the value of **i** farthest removed from European usage; -ĭd approximates closely to the continental îd, —into which it is easily lengthened,—is readily recognised by the foreign ear, is not confused with termination -īte, is in line with present phonetic progress, and has the backing of authority and usage. The short sound of **i** naturally dictates the dropping of the final **e**. ("According to Smart and Cull, chemical terms ending in **-ide**, as bromide, chloride, etc, should be pronounced with **i** long; but all other orthoëpists are unanimous in making the vowel short; and the propriety of the latter mode of pronunciation is established by the fact that this whole class of words is not unfrequently spelt without the final **e**; thus bromid, chlorid."— Webster's Dictionary, edition of 1864 and 1884, Principles of Pronunciation, p. xliv.)

Terminations in **-in.**—In the names of chemical compounds, including all those formerly ending in **-ine** (except the small group of doubly unsaturated hydrocarbons, as propine), this termination is always pronounced -ĭn and is never followed by an **e**. In this case much the same reasons as those given in the preceding paragraph dictate the uniform use of -ĭn, and not only authority, but modern usage is even more fixed in the employ-

[1] Fàte, făt, fär, mēte, mĕt, pine, pĭn, marine, nōte, nŏt, mŏve, tūbe, tŭb, rüle, mȳ, y̆ = ĭ.

ment of the short **i**, so much so that the change practically amounts to simply dropping the final **-e** when following **-in.** The only objection to be raised against the innovation is that based on the recommendation of Watts some few years since, that basic substances should terminate in **-ine** and neutral substances (*viz.*, glycerids, glucosids, proteids, and bitter principles) in **-in.** While this distinction possesses a certain value, it is to be noted that it involves a difference in spelling with little or no difference in pronunciation—a useless and undesirable complication, and out of touch with modern phonetic principles; it demands a very extensive knowledge of the constitution of a large number of compounds with these terminations; it has never been recognised by many chemists; and, finally, while it has been partially adopted by others it has rarely been used consistently.

Terminations in **-meter.**—Words in this class used in the metric system are regarded as compound words, and each portion retains its own accent; as mil'lime″ter.[1] Of the two authorised forms of accentuation, it was deemed better to retain this and exclude completely the other (*viz.*, the uniform laying of the accent on the antepenult), because the former is of help to foreigners using our language and *vice versa*, while the practice accords with the general rule for the retention of the primitive accents in compound words.

Derivatives of *Valence.*—The Latin prefixes are used invariably to the exclusion of the Greek, in accord with the recognised principles of word-building in our language.

Arsin, Stibin, Phosphin, Hydrogen Sulfid.—These shorter terms, long since adopted by many chemists, now supersede completely the cumbersome arsenuretted hydrogen, etc. (It is to be hoped that the simplification may soon be carried a step further by the introduction of sulfin, selenin, and tellurin.)

Gramme.—The retention of the **-me** of the French spelling may seem ill to accord with principles of phonetic reform actuating many of the above changes. It is, however, dictated by reasons of prudence, so long as the metric system is used side by side with the old apothecaries' series of weights and measures by our physicians and pharmacists. When the transition-period is over, and the latter system is effectually displaced, the simpler form will unquestionably be adopted. It is obvious to all that the marked similarity in sound and spelling between the words *grain* and *gram* could easily lead to mistakes of the gravest nature, and as a matter of fact a number of deaths have already been caused by either mere inadvertence or by the omission of the dot over the *i* in *grain.* (*Amer. Druggist*, **20**, 369.)

The following quotation from an article by Professor Edward Hart, in the Journal of Analytical and Applied Chemistry, is of interest in connection with the above:

[1] Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

" These proposed changes were carefully canvassed with those gentlemen who have made the English language their life-study and who were unanimous in favor of them. They were made the subject of a number of reports to the American Association for the Advancement of Science and were favored by a large majority of those present. In drawing up the report the committee sought and obtained the opinions of a number of chemists not members of the Association, and so far as it was possible to obtain an expression of opinion the recommendations voice the wish of American chemists."

In the article from which this quotation is taken occurs the passage : " Man is a conservative animal and does things in a certain way because he is accustomed so to do them. This conservatism increases with age until it becomes almost impossible to shake it off." In the face of these fundamental truths one hesitates to express an opinion on the recommendations of the American Association, fearing that to differ may be to proclaim one's self an ass, and the ass is even more conservative than man. This spelling, as every one knows, is a hard subject to deal with, and the Committee of the American Association deserves much credit for the care they have given to their work. Their recommendations seem on the whole to be wise, and it would perhaps be well if every chemist would adopt them. There is one chemist known to the present writer who is willing to acknowledge that he doesn't like " sulfur," but he is also willing to acknowledge that this is no argument against it.

One of the advantages which the committee mention under the head of -**ic** is " bringing us into accord with the British custom "; and their recommendation as to -**ol** "also is in harmony with British usage and brings about a most desirable simplification and uniformity." If conformity to British usage be advantageous, then why, it may be asked, should we be advised to fly directly in the face of British usage by dropping the final **e** "from all chemical terms formerly ending in -**ide** "? -**id** may be just as good as -**ide**, but is not uniformity worth much ? Then, again, -**ine** has been growing in favor of late years as signifying basic properties, and it seems to the writer that in contracting to -**in** we lose more than we gain by giving up the -**e**. Perhaps a joint committee of the British Association and American Association might reach some conclusions of value. The question as to the use of the final -**e** is, however, one that will not be settled by any committee.

<div align="right">I. R.</div>

THE ACTIVE COMPONENTS OF INACTIVE LACTIC ACID.

In 1884 Lewkowitsch [1] stated that a solution of ammonium lactate becomes dextro-gyratory after having been subjected to the action of *Penicillium glaucum.* The work of Linossier, pub-

[1] Ber. d. chem. Ges. **16**, 2720.

lished in 1891,[1] was a repetition and extension of that of Lewkowitsch, but led him to the conclusion that the salt solution becomes laevo-gyratory through the action of the ferment, and that from this solution a dextro-gyratory lactic acid can be obtained. On the other hand, Schardinger[2] obtained a laevo-gyratory lactic acid by the bacterial decomposition of cane-sugar. This acid formed a zinc salt of the same composition as that of sarcolactic acid, and when these two salts were mixed in equal quantities in solution it was found that ordinary zinc lactate crystallised out. It remains for us now to notice that Purdie and Walker[3] have succeeded in separating, by means of the strychnine salts, the two active varieties of lactic acid from the inactive variety, and have shown that they possess equal and opposite optical activity.

In experimenting with alkaloid salts, cinchonine and narcotine were employed with little or no success. On the other hand, on fractional crystallisation of a neutral solution of strychnine in pure lactic acid, salts were obtained which in solution exhibited optical activity. The least soluble salt was dextro-rotatory; from this a laevo-rotatory acid was set free, and from this in turn the zinc salt was prepared. This last should possess, according to analogy, the same composition and chemical properties as the well-known zinc sarcolactate. The composition of the two was in fact shown to be identical, and to differ from that of the ordinary zinc lactate in containing one less molecule of water. The solubility of zinc laevo-lactate in water was shown to be practically identical with that of the sarcolactate; the same statement may be made with respect to their respective rotatory powers.

An examination of the free laevo-lactic acid showed that, like sarcolactic acid, this acid rotates the plane of polarisation in one direction, while its salts rotate it in the other. Like sarcolactic acid, it readily forms an anhydride whose activity is in the opposite sense to that of the acid. The acid was shown to be identical with Schardinger's.

From the more soluble strychnine lactate crystals a zinc dextro-lactate was prepared identical with zinc sarcolactate; from this salt sarcolactic acid could be isolated.

From the two lactic acids thus obtained, isomeric zinc-ammonium salts were prepared, alike in all but the direction of their optical activity.

A confirmatory experiment was made as follows: Equal weights of the two active zinc salts were mixed in solution, and pure, absolutely inactive zinc lactate crystallised out.   W. W. R.

[1] Bull. Soc. chim. (Paris), [3] **6,** 10; Abstr.—Ber. d. chem. Ges. **24,** (c) 660.
[2] Monatsh. Chem. **11,** 545; Abstr.—This Journal **13,** 277; J. Chem. Soc. **60,** 666.
[3] J. Chem. Soc. **61,** 754.

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want to know, and tells him this clearly. He also, undoubtedly,

tells him much that will have no "practical" value, and some of this will, perhaps, look strange and uninviting; but this will be of special value to many, and of some value even to those who do not understand it, for it is well for us all at times to be forcibly reminded of our own ignorance.

There are some interesting revelations as regards adulterations of coffee and tea. Magnetic iron ore and brass-filings are among the pleasant things mentioned as adulterants of tea. Under coffee we are told of all sorts of things, and this passage is not surprising: "The diminished consumption of coffee in England is doubtless largely due to the frequency and extent of its sophistications." I. R.

CHEMICAL LECTURE EXPERIMENTS; NON-METALLIC ELEMENTS. By G. S. NEWTH, Chemical Lecture Demonstrator in the Royal College of Science, South Kensington. Longmans, Green & Co., London and New York, 1892. vi & 320 pp. 8vo.

Here is a book that will bring joy and consolation to many. It is unquestionably an improvement, and a great improvement, upon its predecessors. On almost every page even the experienced lecturer will find something suggestive, either an old experiment in new form or a new experiment. It is certain that of the experiments many will be new to some and some will be new to many. The descriptions are clear and give one confidence; and the drawings of apparatus are all new "with the exception of three." They represent apparatus actually used to-day, not antiquated forms. This use of new drawings gives the book a fresh appearance and lures one on to read, and the more one reads the better he is pleased. The author tells us that "no account of any experiment has been introduced into the book upon the authority solely of any verbal or printed description, but every experiment has been the subject of my personal investigation."

While primarily intended for teachers, the book will also be found useful by students. In what way, can best be indicated by the author's own words. "Secondly," he says, "it is my object to furnish the chemical student with a book which shall serve as a companion to the lectures he may attend—a book in which he will find fully described most, if not all, of the experiments he is likely to see performed upon the lecture-table, and which will therefore relieve him from the necessity of laboriously noting them and often sketching the apparatus used. In this way the student will be spared much unnecessary and distracting work during the lecture, and will therefore be better able to give his undivided attention to the explanations or arguments of the lecturer."

The "wire-gauze spoon" method of collecting hydrogen from the action of sodium upon water is gone, it is to be hoped never

to return. In its place a simple and ingenious device appears which deserves to be widely known, as it will contribute to the peace of mind of many lecturers. The author says it "is the best method, and the only one which is free from danger." It is thus described: "A piece of ordinary lead or composition pipe, about 25 millimetres long and about 4 millimetres bore, has one end closed by squeezing in a vice, or by a few taps with a hammer. A pellet of sodium is rolled between the fingers and pushed into this tube. It may well be forced in by pressing the mouth of the tube down upon the table, the excess of the metal being afterwards trimmed off with a knife. This tube with its contents is then dropped into the pneumatic trough, in which it will sink, and hydrogen will be evolved in a steady and gentle stream. . . . If the little tubes are filled as described, it is impossible for any explosion to take place in the performance of this experiment. The filled tubes may be preserved in naphtha." A detailed description of the method of sealing bulbs containing a mixture of hydrogen and chlorine is given, and no doubt many will be glad to get this information. Among the many other good experiments presented the following may be specially mentioned: one showing the combustion of ammonia in oxygen; the liquefaction of ammonia by cold and pressure; freezing water by solid mercury; the preparation of nickel carbonyl, $Ni(CO)_4$; many experiments on flames, etc., etc.

Excellent instructions are given in connection with many of the experiments for the use of the lantern; and a special section of the book is devoted to "Lantern Illustrations." In an "Appendix," finally, a number of valuable tables are given. I. R.

THE CHEMICAL BASIS OF THE ANIMAL BODY.—An Appendix to Foster's Text-Book of Physiology. Sixth Edition. By A. SHERIDAN LEA, University Lecturer in Physiology in the University of Cambridge. New York and London: Macmillan & Co., 1893. 288 pp. 8vo.

While this book is chiefly interesting to physiologists, chemists who wish to inform themselves concerning the substances that enter into the composition of the animal body will find it of value. The trouble with most books of the kind is that they bear unmistakable evidence of having been written by physiologists whose knowledge of chemistry is deficient. But in the present case we are informed that the author is "indebted to Dr. S. Ruhemann for reading the proofs from page 91 to page 216, in which the text contains many formulae, and involves special chemical knowledge." As Dr. Ruhemann is a chemist, the result is that the book is free from chemical solecisms, and the chemist can read it without having his prejudices stirred up. Due attention is given to the researches of Emil Fischer in the sugar-group, to the

conceptions of stereo-chemistry as illustrated in the lactic acid group, and to the constitution of uric acid and related substances. Of course, the rôle played by chemical substances in the body is the point of interest to the physiologist, and the results of investigations bearing upon this subject appear to be well summed up. A good example of this is found under urea. First, the chemistry of this compound and its most important derivatives is given; then, analytical methods applicable to it; then, the methods of synthesis; and, finally, a full discussion, based upon established facts, of the part played by urea in the body. Wöhler's epoch-making discovery of the conversion of ammonium cyanate into urea acquires new interest in the light of the following remark: "In other words, ammonium cyanate is a type of living, and urea of dead nitrogen, and the conversion of the former into the latter is an image of the essential change which takes place when a living proteid dies." The meaning of this sentence is not, to be sure, quite clear without the context. With this, it is highly suggestive. As regards the importance of chemical study to the physiologist the author says: "The physiological function of any substance must depend ultimately on its molecular (including its chemical) nature; and though at present our chemical knowledge of the constituents of an animal body gives us but little insight into their physiological properties, it cannot be doubted that such chemical information as is attainable is a necessary preliminary to all physiological study."			I. R.

BERZELIUS UND LIEBIG. Ihre Briefe von 1831-1845 mit erläuternden Einschaltungen aus gleichzeitigen Briefen von Liebig und Wöhler sowie wissenschaftlichen Nachweisen herausgegeben von JUSTUS CAR-RIÈRE. 1893. München und Leipzig: Lehmann. vii und 280 pp. 8vo.

It is fortunate for the chemical world that in the early part of this century letter-writing was not a lost art and that value was attached to letters. For the chemist, there is hardly a more interesting book than that which a few years ago brought before us the letters of Liebig and Wöhler. And now we have another treat in this small volume of the letters of Liebig and Berzelius, which we owe to a grandson of Liebig who began at an early age to collect letters for the sake of the autographs. Anything written by these great men in regard to their work must be read with interest and profit by the present generation. This is the very heart of history, and one feels it throb as one reads.			I. R.

AMERICAN

CHEMICAL JOURNAL.

THE ACTION OF METALS ON NITRIC ACID.

I.—The Reduction of Nitric Acid by Copper.

By Paul C. Freer and Geo. O. Higley.

Although considerable work has been done on this subject, yet in no case has an attempt been made to isolate all the products of reduction. In 1842 Millon[1] undertook to ascertain the temperature at which pure nitric acid, of varying degrees of concentration, acts upon metals. He found that an acid having a specific gravity of 1.07 does not attack copper at 20° C., but that, upon the addition of a little nitrite of potassium, action immediately begins, and from this he concluded that in the reduction nitrite of copper is first formed, the latter being subsequently decomposed by the nitric acid. This author thereupon suggested that the action of the small quantity of nitrous acid present is comparable to that of a ferment. Millon also discovered that an acid of 1.217 specific gravity began to act upon copper at a temperature as low as —10°, while that of 1.108 attacked the metal only above —2°. From a qualitative study of the products Millon concluded that they depended on: 1. Concentration of acid; 2. temperature; 3. the presence of nitrogen dioxide; and 4. solubility of the products.

At a somewhat later period Gay Lussac[2] disputed Millon's statements, showing that nitric acid, even of a specific gravity of 1.02, attacks copper at a temperature as low as —12°. In some

[1]Ann. chim. phys. [3], 6, 95.   [2] Ibid. [3], 6, 385.

further experiments this chemist added sulphuric acid of a strength represented by the formula $H_2SO_4 + 9H_2O$ and nitric acid of a specific gravity of 1.07, respectively, to copper in two test-tubes, placed both in a freezing mixture, and thus found that there was no action in either case until nitrogen dioxide (hyponitric acid) was added, whereupon both reacted with equal energy, and therefore Gay Lussac concluded the experiment proved simply that "hyponitric acid" is less stable than nitric acid, and ridiculed Millon's idea of metallic fermentation. His work, like Millon's, was mainly qualitative. It is our own experience that nitric acid, entirely free from lower oxides, of a specific gravity as low as 1.20, reacts with pure copper with the greatest readiness.

In 1871 Bourgoin[1] proved that electrolysis of very dilute nitric acid causes no reduction, hydrogen being evolved at the negative pole. With an acid $HNO_3 + 6.25aq.$, hydrogen is first evolved, this is followed by nitrogen, while, finally, ammonia is produced, and with $HNO_3 + 19aq.$, hydrogen and subsequently nitrogen are obtained; the latter gradually increasing in quantity, attaining a maximum and, in the end, disappearing. No nitrous oxide could be detected. When, in subsequent experiments, a more concentrated solution was employed, no hydrogen was at first evolved; however, a blue coloration, probably due to nitrous acid, was observed around the negative pole; finally, the electrolysis of $HNO_3 + 1\frac{1}{2}aq.$ produced pure nitric oxide for a time and, afterward, a mixture of hydrogen and nitric oxide.

In 1875 Acworth[2] made a series of quantitative experiments with the view of determining the proportions of nitric oxide, nitrous oxide and nitrogen which are formed at different stages of the solution of copper in nitric acid, but no attempt was made to estimate the trioxide and dioxide of nitrogen produced, nor was any investigation of the effect of temperatures, above the ordinary, undertaken. The conclusions of this investigator were:

1. Cold, dilute nitric acid, acting on copper, gives almost pure nitric oxide, the gas containing 90–95 per cent. of that substance, but, with increase of copper nitrate in the solution, the per cent. of nitric oxide diminishes.

2. If a concentrated solution of copper nitrate is added to the acid at the beginning of the experiment, 85 per cent. of the evolved gas is nitrous oxide.

[1] Journ. Pharm. [4], **13**, 266–270.   [2] J. Chem. Soc. **18**, 828.

3. Potassium nitrate in solution has little or no effect on the composition of the gas.

4. Ammonium nitrate solution, when added, causes the evolution, chiefly, of nitrous oxide and nitrogen.

5. Zinc, mercury or iron, when treated with nitric acid and ammonium nitrate, chiefly evolve nitrogen.

A little later, Acworth and Armstrong[1] published a paper containing an account of work done by them in the same general direction. This research, however, was more complete, because the action of several metals was investigated, and, in addition, some experiments were made on the effect of temperature, as well as an attempt to account for the whole of the metal employed. This work is, however, open to criticism in several respects:

1. The temperature was not kept constant during the solution of the metal, even in those experiments in which the effect of temperature was to be determined.

2. The liquid was not agitated while the action was in progress, although it is a well-known fact that, when quiet, a distinct layer of the nitrate is formed about the metal, thus changing the conditions of the reaction. Indeed, Acworth himself had previously shown that copper nitrate, when present in the mixture, increases the per cent. of nitrous oxide formed.

3. No attempt was made to determine the amounts of dioxide and trioxide of nitrogen, although these gases are the sole products of the reduction of 1.40 nitric acid by copper. One would think that an evolution of only about two cubic centimeters of gas, by the solution of 350 milligrams of copper, should have led to an investigation of the other substances produced by the reduction; to our minds, the study of the minor products of a reaction, while the major ones are entirely neglected, is of little or no value. Of course, since the relative amount of gaseous products increases as the acid is diluted, this criticism will not apply with equal pertinency to the determinations made with an acid containing a considerable quantity of water. In several other respects, also, Acworth and Armstrong's work seems to us to be very incomplete.

At a date later than that of Acworth and Armstrong's work, Gladstone and Tribe[2] published a very interesting paper on the action of the zinc-copper couple on potassium nitrate, potassium chlorate, etc. The action was shown to be electrolytic, the reduc-

[1] J. Chem. Soc. **32**, 54.   [2] *Ibid.* **33**, 139.

tion taking place in the immediate vicinity of the negative metal ; the conclusion arrived at being that the hydrogen is probably condensed by the finely divided copper previous to entering into the reaction.

In 1883, Divers[1] did some work in which he showed that metals which are acted upon by nitric acid may be divided into two classes. The metals of the first class (copper, silver, bismuth and mercury), when treated with nitric acid, form neither ammonia nor hydroxylamine, while those of the second class (including tin, magnesium, zinc, cadmium, aluminium and iron) produce ammonia or hydroxylamine, or both. Upon rather slender experimental evidence, Divers has attempted to deduce reasons for a structural formula for nitrous acid and its salts, in which he supposes hydrogen, respectively metal, to be joined to nitrogen ; the conclusions which he reaches, however, do not seem to us to follow as a logical result of his work.

A study of the literature of this subject reveals the fact that no investigator has quantitatively determined all of the products of the reduction of nitric acid by metals. Only Acworth and Armstrong have attempted to account for all of the metal dissolved, and even in their results there is a discrepancy of 20 per cent. or more between the equivalent of the products obtained and the weight of metal employed. We, therefore, propose to once more take up the question of the reduction of nitric acid by metals, and, by an improved method, hope to throw additional light upon these complicated reactions.[2]

The first series of reactions which we have undertaken to study is that arising from the action of copper on nitric acids of varying degrees of concentration, and, after repeated variations in our method, we have finally constructed a comparatively simple apparatus which gives satisfactory results.

Experimental Part.

Our apparatus consists of a 200-cc. flask, having a ground-glass cap perforated by three tubulures. Into one of these is fitted a dropping-funnel to contain the acid, and having a three-way stop-

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[1] J. Chem. Soc. **43**, Trans. 455.

[2] It is obviously too early in the research for us to enter upon a discussion of the bearing which our work has upon the question of nascent action ; we intend, however, to critically examine this subject after all of our experimental work has been completed.

a, Dropping funnel for HNO₃.　　*b*, Three-way stop-cock.　　*c*, Stirring rod.　　*d*, Tube filled with glass wool.　　*e*, Winkler spiral tube.
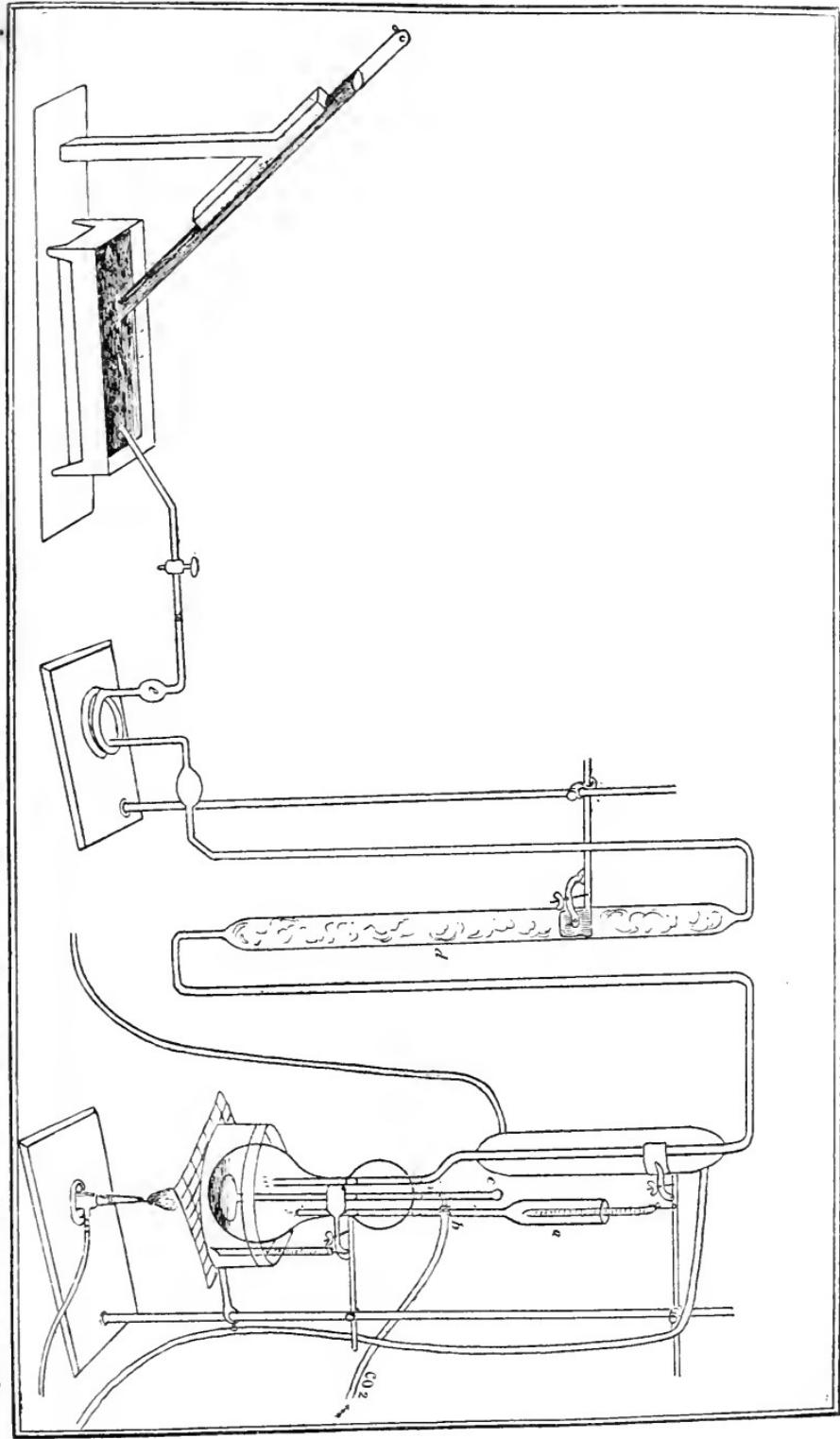
cock which connects with an apparatus furnishing pure carbon dioxide; the central tubulure is provided with a glass rod carrying a platinum disk for stirring the liquid; the third connects with a Liebig's condenser. The gases pass from this through a long tube filled with glass wool, interposed to remove traces of nitric acid which may be mechanically carried over. A Winkler's spiral tube (containing 35 cc. of pure sulphuric acid, specific gravity 1.84, saturated with nitrous oxide) is attached to absorb nitrogen trioxide and dioxide, the remaining gases passing on to be collected over mercury.

Half a gram of pure copper foil [1] is placed in the flask and then all air expelled from the apparatus by means of a current of carbon dioxide; the flask is at the same time heated to the desired point on a water-bath, after which 15 cubic centimeters of pure nitric acid of the same temperature as the metal is allowed to flow in from the dropping-funnel. During the reaction the liquid is stirred and the temperature carefully regulated until solution is effected; carbon dioxide is now once more admitted, and the flask heated to 100° for one hour, the lower oxides of nitrogen, which are quite soluble in nitric acid (sp. gr. 1.40), being thereby all swept on into the Winkler tube. The contents of the latter are now washed with concentrated sulphuric acid into a graduate, and by addition of a further quantity of that acid the volume is brought up to 100 cubic centimeters, and then the amount of nitrosylsulphuric acid is determined by titration with decinormal permanganate solution. In performing this operation, the best results have been obtained by adding the acid solution to the permanganate, according to the method of Lunge.[2] The total nitrogen is afterward determined as nitric oxide by analysing a portion of the nitrosylsulphuric acid solution over mercury in the nitrometer.[3] From the results obtained in these two operations, the quantity and proportions of nitrogen trioxide and dioxide can be calculated,[4] as is shown below. The nitrous oxide, nitric oxide and nitrogen which have been collected over mercury in the eudiometer tube, are analysed as follows:

The nitric oxide is determined by addition of oxygen with absorption of the excess of the latter by pyrogallol; the nitrous

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[1] The foil used in many experiments was very thin and proved itself to be chemically pure. We have also made a series of determinations, using copper wire of 2 mm. diameter, and so discovered that the shape of the copper has no influence on the course of the reaction.

[2] Ber. d. chem. Ges. **10**, 1073.   [3] *Ibid.* **11**, 438.   [4] *Ibid.* **12**, 357.

oxide is estimated by explosion with hydrogen, and the nitrogen determined by difference.

While we have made a number of determinations with a more dilute acid, when we always obtain considerable nitric oxide, most of the work which has thus far been completed has been done with an acid having a specific gravity of 1.40; with this concentration the reduction-products determined as shown above, have proved to be exclusively trioxide and dioxide. It being possible, however, that some nitric oxide might have been formed in the reaction but subsequently absorbed by the nitrosylsulphuric acid (which, by reason of the reaction between sulphuric acid and nitrogen dioxide, must contain some nitric acid), several determinations were made with the purpose of ascertaining the percentage of absorption of nitric oxide in nitrosylsulphuric acid containing nitric acid.[1] Pure nitric oxide was therefore passed through a Winkler's spiral tube containing 30 cubic centimeters of sulphuric acid to which had been added 0.0895 gram of nitrogen trioxide and 0.0754 gram of nitric acid, the unabsorbed portion of the gas being collected over mercury and the per cent. of loss determined. Two experiments gave the following results:

    I.   30.65 cc. lost 19.99 cc.; an absorption of 34.78 per cent.

    II. 27.65 cc. lost 18.13 cc.; an absorption of 34.43 per cent.

Obviously, the conditions in these experiments were much more favorable for the absorption of nitric oxide than those which obtain in our ordinary determinations, because in the former there is present from the beginning a considerable mass of nitric and nitrosylsulphuric acids, while in the latter neither is formed in any quantity until the operation has proceeded for some time, the mass present increasing steadily during the reaction. It is to be presumed that, were nitric oxide formed at all, it would pass off among the first reduction-products. It is nevertheless necessary, in order to ascertain whether any nitric oxide is possibly produced during the solution of copper in a great excess of nitric acid having a specific gravity of 1.40, to conduct the experiment with an apparatus which does not necessitate the use of sulphuric acid, and, therefore, we made several determinations with our usual apparatus, substituting, however, for the Winkler tube, three con-

[1] That nitric oxide is somewhat soluble in nitrosylsulphuric acid has already been proven. Ber. d. chem. Ges. **11**, 1643. Veley (Proc. Roy. Soc. **52**, 272) has also recently shown that nitric oxide is quite readily oxidised by means of concentrated nitric acid.

densation-tubes [1] (which together gave a cooling length of about 75 centimeters), kept at a temperature of —20°. By this means, nitrogen trioxide and dioxide were condensed to liquids, and in no case did any appreciable amount of gas (nitric oxide, nitrous oxide and nitrogen) pass on to be collected. The sole products of reduction of nitric acid (sp. gr. 1.40) by copper are, therefore, nitrogen trioxide and dioxide.

CALCULATIONS.

The formation of nitrosylsulphuric acid from nitrogen trioxide and dioxide, respectively, may be represented by the following equations:

(1) $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + N_2O_3 + 3H_2O$;

(2) $N_2O_3 + 2H_2SO_4 = 2SO_2 \left\{ \begin{array}{l} OH \\ NO_2 \end{array} + H_2O ; [2] \right.$

and from the dioxide:

(3) $2Cu + 8HNO_3 = 2Cu(NO_3)_2 + 4NO_2 + 4H_2O$;

(4) $4NO_2 + 2H_2SO_4 = 2SO_2 \left\{ \begin{array}{l} OH \\ NO_2 \end{array} + 2HNO_3. [3] \right.$
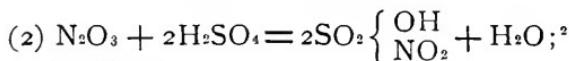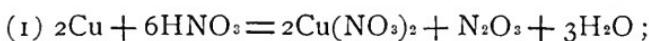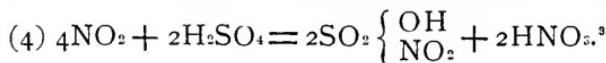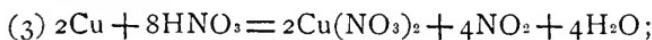
It follows, then, that the same amount of nitrosylsulphuric acid is produced from the solution of a given weight of copper in nitric acid whether the reduction-product is the trioxide, the dioxide, or a mixture of the two. We see, however (equation 4) that when nitrogen dioxide reacts with sulphuric acid, *one-half of the nitrogen forms nitric acid*, but with the trioxide *nitrosylsulphuric acid alone* is produced; so that when a determination of total nitrogen in the solution is made in the nitrometer, and the result is calculated as trioxide, for the purpose of comparison, the excess in weight of the latter over the weight of trioxide, determined with permanganate, is equivalent to the nitric acid which was present as such in the Winkler tube, and is, therefore, equivalent to one-half the nitrogen dioxide which has reacted upon the sulphuric acid.

Let a represent the weight of N_2O_3 from the nitrometer analysis, and let b represent the weight of N_2O_3 obtained by titration with permanganate; then $2(a-b)$ represents the trioxide

[1] It seems scarcely necessary to mention that the condensation-tubes were fused together so as to avoid rubber connections.

[2] Graham-Otto: Lehrbuch, Vol. I, 657.

[3] Ann. Chem. (Liebig) **122**, 19. *Ibid.* **125**, 293.

equivalent of the dioxide, and $2(a-b) \frac{2058}{1701}$[1] $=$ weight of dioxide produced; $a - 2(a-b) = 2b - a =$ weight of trioxide, as such.

If $a = b$, then the reduction-product is trioxide only.

If $a = 2b$, then the product is dioxide only.

RESULTS.

Our results, so far as obtained in experiments with acid having a specific gravity of 1.40, are given in the appended table. Experiments 1–3 were made with an apparatus having three short rubber connections, which were coated inside with paraffin, but as, in every case, these connections were slightly attacked by the oxides of nitrogen, there was a consequent loss of reduction-products. We, therefore, so modified our apparatus as to entirely eliminate rubber connections, all parts being fused together except the joint between the glass wool and Winkler tubes, which latter was made by pushing one tube within the other and then sealing the joint with high-melting paraffin. It is for this reason that the first three experiments account for but from 95 to 98 per cent. of the copper, but certainly the last four results, with a variation of only from 100.03 to 100.33 per cent. of the copper, leave nothing to be desired and fully demonstrate the success of our apparatus.

xpt.	Copper. Mgrs.	Acid. Sp. Gr.	Vol. cc.	T	Mgrs. N_2O_3. Winkler Tube. Calc.	Found.	Per cent. of Copper accounted for.	Nitrometer. Corrected Vol. NO.	Equiv. in N_2O_3.	Percentage Composition of Gases. N_2O_3.	NO_2.
1	500	1.40	15	50°	300.33	285.83	95.1	294.8	501.45	11.9	88.1
2	"	"	"	25°	"	290.3	96.6	290.2	493.65	15.1	84.9
3	"	"	"	25°	"	294.6	98.09	298.4	507.5	13.4	86.6
4	"	"	"	0°	"	301.33	100.33	*			
5	"	"	"	0°	"	300.42	100.03	314.	534.1	9.4	90.6
6	"	"	"	10°	"	301.133	100.26	325.0	552.8	7.5	92.5
7	"	"	"	25°	"	300.79	100.15	*			

*No nitrometer determinations in these two experiments were made, the object being only to account for copper dissolved, as reduction-products.

As regards the ratio between the trioxide and dioxide, however, there is some variation, possibly due in part to varying amounts

[1] One cubic centimeter of NO weighs .001343 gram and is equivalent to .001701 gram N_2O_3 or to .002058 gram NO_2.

of nitric acid which are mechanically carried over by the gases. Control tests, made without the copper, by heating 15 cc. of 1.40 nitric in the flask at 100° for one and a half hours, and then passing a current of carbon dioxide, showed only traces of nitric acid in the Winkler tube, by means of the ferrous sulphate test, and none whatever with the nitrometer ; when the trioxide and dioxide are generated, however, they may carry over appreciable amounts of nitric acid, and we therefore purpose adding a much longer tube filled with glass wool, with the hope of entirely eliminating this possible source of error ; it is not at all improbable, however, that there may be some variation in the natural course of the reaction.   Experiments made since the introduction of this modification in the apparatus have demonstrated that the slight variations are not due to the mechanical addition of nitric acid.

CONCLUSIONS.

1. The sole products of reduction of excess of nitric acid, specific gravity 1.40, by copper, are nitrogen trioxide and dioxide; the proportions being about 10 per cent. of the former to 90 per cent. of the latter.

2. The effect of varying temperature upon the proportion of the reduction-products is, apparently, but slight.

Now that an apparatus is completed and satisfactory results have been obtained, we intend to continue the research, to study all the effects of dilution and temperature on the nature and proportion of the reduction-products, extending the work so as to include a number of other metals besides copper, as well as the effects of nitric acid on substances such as cane-sugar starch and arsenic trioxide.   We hope by publishing this preliminary article on a portion of the work already accomplished, to reserve this field for ourselves.

Since writing the above, two articles by C. Montemartini[1] have appeared, treating the same subject.   The above author has dissolved zinc, iron, cobalt, nickel and cadmium in nitric acid of differing specific gravity, obtaining, in each case, ammonia, nitrous acid, nitrous oxide, nitrogen and nitric oxide, but in each case the reduction-products are considerably in excess of those calculated. Montemartini has also studied the action of nitric acid upon zinc,[2] determining the degree of concentration and temperature at which

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[1] Gazetta Chim. **22**, I, 250-265.   [2] *Ibid.* 274-343.

a maximum of each reduction-product is produced. The velocity of action between zinc and nitric acid increases regularly with the concentration up to 25 per cent. acid, remains constant between 33 and 42 per cent. and then diminishes regularly, with a minimum at 68 per cent. Montemartini concludes that nitric oxide is always a product of secondary reaction. Our results with copper are certainly more accurate than Montemartini's with zinc, for the fact that the latter investigator always obtains an excess of reduction-products over the calculated quantity still remains to be accounted for; our method seems, therefore, better calculated to lead to trustworthy results than his.

The objection may possibly be advanced that, although we have proven that nitrogen trioxide and dioxide are the sole tangible products of the reduction of concentrated nitric acid by copper, nitric oxide may, nevertheless, be at first formed, to be subsequently oxidised by the excess of nitric acid. In order to ascertain the validity of such a criticism we have performed the following experiment: Five hundred mgr. of copper were placed in the flask of our apparatus and nitric acid was then added, drop by drop, sufficient time for all reaction to cease being allowed between the additions, and this process was continued until all copper was dissolved. By this means an excess of nitric acid was never present, but, nevertheless, no nitric oxide was produced. The conclusion is inevitable, therefore, that the nitric oxide formed when using dilute acid is solely the product of secondary reactions.

MIXED DOUBLE HALIDES OF LEAD AND POTASSIUM.

By Charles H. Herty.

Introduction.

Up to the present, but little work seems to have been done on the subject of mixed double halides. Atkinson[1] describes a salt of antimony, potassium, chlorine and bromine, to which he gives

[1] Jour. Chem. Soc. **43** (1883), 289.

the formula $K_3SbCl_3Br_3.1\frac{1}{2}H_2O$. He also obtained salts corresponding to the formulas $Sb_2Cl_6Br_3K_3.2H_2O$ and $SbCl_3BrK.H_2O$. Pitkin[1] describes the salt $2KBr.PtCl_4$.

Remsen and Richardson,[2] during the course of an investigation of the double halides of tin, made some experiments on compounds of stannous bromide with potassium chloride. Their experiments were limited by a lack of time, and the conclusions drawn necessarily unsatisfactory. Although they describe a salt corresponding closely in composition to the formula $K_2SnCl_2Br_2.$ $2H_2O$, yet from other experiments they were led to believe that another compound which they obtained was "a mixture of the two salts $KSnBr_3.H_2O$ and $KSnCl_3.H_2O$." Recently Wells[3] has published an account of several mixed double halides of caesium and mercury.

As no work has been done on the mixed double halides of lead and potassium, the following investigation was undertaken in the hope of obtaining such compounds as $KPbI_2Br$ ($PbI_2.KBr$), $KPbI$ Br_2 ($PbBr_2KI$), etc. As a result of this investigation, it has been shown conclusively that the compounds formed by dissolving lead iodide in an aqueous solution of potassium bromide are mixtures of the salts $KPbI_3$ and $KPbBr_3$, confirming thus the suggestion of Remsen and Richardson.

Method of Analysis.

The method of analysis used in determining the composition of these isomorphous mixtures is based upon the fact that when lead iodide or lead bromide is heated in contact with a solution of sodium carbonate, all of the lead is converted into lead carbonate, while the halogen passes into solution as the sodium salt. The details of the method are as follows :

1. A weighed quantity of the powdered substance, about 1 gram, is heated for two hours at a temperature of 110°. From the loss of weight, water of crystallisation is calculated.

2. The substance, after being thoroughly moistened with water, is transferred to a beaker, and upon it is poured about 25 cc. of water previously boiled in order to expel all carbon dioxide. To this mass is then added a solution of sodium carbonate containing slightly more of the salt than is sufficient to convert all of the lead present into lead carbonate. A gentle heat is then applied for

[1] Chem. News **47**, 118.   [2] This Journal **14**, 96.   [3] Amer. Jour. of Science **44**, 232.

several hours. The white precipitate which appears on first add-
ing the solution of sodium carbonate is due to the precipitation of
the small quantity of lead held in solution by the potassium iodide
and potassium bromide present. The solid matter in the beaker
soon loses its yellow color and becomes white as the lead is
gradually converted into carbonate. The small lumps of lead iodide
are broken up by pressing with a glass rod flattened at the end.
After the yellow color has disappeared, the heating is continued for
one-half hour, in order to insure the conversion of all lead into the
carbonate. After cooling, the liquid is filtered off by means of a
filter-pump, and the lead carbonate is thoroughly washed with
boiled water. Dilute nitric acid is then slowly added to the lead
carbonate on the filter, and the lead nitrate washed through the
filter, and the lead estimated by precipitation as sulphate.

3. The filtrate from the lead carbonate is heated to boiling and
acidified with dilute nitric acid. If the solution now has a yellow
tint, the color is removed by adding a few drops of sulphurous
acid. Silver nitrate solution is then added in slight excess. After
standing twenty-four hours the solution is filtered off, and the pre-
cipitate of silver iodide and silver bromide is dried and weighed.
The silver salts are then fused in a current of chlorine until a con-
stant weight is attained, and the bromine and iodine estimated in
the usual way.

4. In the filtrate from the silver iodide and silver bromide the
excess of silver is removed by precipitating with dilute hydro-
chloric acid and filtering after standing twenty-four hours. This
last filtrate is then evaporated to dryness, the dry residue moist-
ened with concentrated hydrochloric acid to insure complete con-
version into chlorides of sodium and potassium, and heated again
until the mass is thoroughly dry. In the residue the potassium is
then determined in the usual manner by conversion into potassium
chlorplatinate.

If to a solution of lead iodide or bromide in potassium iodide or
bromide sodium carbonate solution be added, all lead is precipi-
tated quantitatively as lead carbonate. This fact furnishes a means
for determining the composition of the mother-liquors from which
the various compounds described below crystallise. The details
of the method are as follows:

1. A portion of the solution, about 5 cc., is drawn off into a
weighed porcelain crucible, and the weight of the whole is quickly

determined.   The solution is then evaporated to dryness, and the crucible heated for several hours at a temperature of 110°.   From the loss in weight, water is calculated.

2. About 5 cc. of water is then added to the residue in the crucible, and heat applied until all dissolves.   Sodium carbonate solution is then added until all lead has been precipitated.   The contents of the crucible are now washed into a beaker, diluted with water and allowed to settle.   The clear solution is filtered off from the lead carbonate.   The lead is then determined as sulphate in the manner described above.

3. The filtrate from the lead carbonate is made up to a volume of 500 cc., and in 100 cc. of this solution, iodine, bromine and potassium are determined as described above.

Experimental Part.

Preliminary Experiments.—For the preparation of mixed double salts, the first method which suggested itself was that based upon the solution of lead halides in water-solutions of the alkaline halides.   Accordingly, preliminary experiments were made in order to determine what combination of halides furnished the best means for studying the problem.   Three portions of a cold saturated solution of potassium iodide were heated almost to boiling; to one was added lead bromide, to another lead chloride, and to another lead fluoride.   The lead salts dissolved in each case, and, on cooling, yellowish needles crystallised from each solution in large quantities.   During crystallisation a great deal of the water present was taken up as water of crystallisation.   This caused so great a concentration of the solution that cube-shaped crystals of potassium iodide crystallised along with the yellow needles.   No definite idea of the composition of the yellow needles could therefore be obtained.   The compound obtained by solution of lead bromide in potassium iodide seemed to be least contaminated by free alkaline halide, and also to have the most perfect crystalline form, and it was therefore decided to confine attention to the preparation of potassium bromiodoplumbites.

Solution of lead bromide in potassium iodide. — A solution of potassium iodide was prepared, of such a strength that 50 cc. of the solution contained 50.8214 grams of potassium iodide.   One portion of this solution, 50 cc., was heated to boiling, and 20 grams of lead bromide added.   The white lead bromide became yellow as

soon as it came into contact with the potassium iodide solution. All dissolved except a very slight white residue. The solution was then filtered from this residue through a hot funnel into a hot beaker, and allowed to cool. Almost immediately crystals began to form. These crystals are needle-shaped and have a yellow tint. They group themselves in small bundles or sheaves. So great was the quantity of crystals that the mass soon became almost solid. The mother-liquor was removed by the aid of a filter-pump, and the crystals dried by pressing between folds of drying-paper. The crystals were labeled *A*.

To a second portion, 50 cc., of the potassium iodide solution, after heating, was added 10 grams of lead bromide. Crystals similar to *A* were obtained, though not in such large quantities. These were labeled *B*.

Still a third crop of crystals was obtained by dissolving 5 grams of lead bromide in 50 cc. of the heated potassium iodide solution. These crystals, labeled *C*, were similar in appearance to *A* and *B*, but the yield was much smaller.

Three portions, 50 cc. each, of the potassium iodide solution were then diluted, each with 50 cc. of water, and heated to boiling. To one of these portions was added 20 grams of lead bromide. The salt turned yellow, as above, but quite a large quantity failed to dissolve. After filtering from this undissolved portion, crystals were obtained from the solution similar to those prepared by using the more concentrated solution of potassium iodide. These crystals were labeled *A'*. To another portion of the diluted solution was added 10 grams of lead bromide. Practically all dissolved, and the needle-shaped crystals obtained on cooling were labeled *B'*. To a third portion of the diluted solution was added 5 grams of lead bromide. Crystals similar to the above were again obtained. These crystals were labeled *C'*.

10 grams of lead bromide were then added to 50 cc. of the concentrated solution of potassium iodide, but no heat applied. Some of the lead salt passed into solution on stirring the mass well, but some, having been changed to yellow lead iodide, remained undissolved. At the same time a white flocculent substance was formed just above the undissolved lead iodide, but it was found impossible to separate accurately the one from the other, so the mass was discarded. The supernatant liquid, however, gave birth to a small quantity of needle-shaped crystals (designated *D*)

after standing twenty-four hours, but the quantity was not sufficient for analysis. 50 cc. of water was then added to 50 cc. of the potassium iodide solution, and 10 grams of lead bromide added in the cold. The lead bromide immediately became yellow, showing the change to lead iodide, and now, after constant stirring, all of the lead iodide disappeared, and in its place was quite a large quantity of a flocculent, white substance, similar to that obtained in the preceding experiment. This salt was dried and labeled X.

In the mother-liquor from X there crystallised, on standing over night, very long, slender needles. These were labeled D'.

To each of the mother-liquors from A, B, C and D was then added 50 cc. of water. All were stirred thoroughly and allowed to stand. Large quantities of needle-shaped crystals separated in each case, and were labeled respectively F, G, H and E.

To the mother-liquors from A', B', C', D', E, F, G and H, water was added until the point of decomposition of the solution with setting free of lead iodide was almost reached. This was done by drawing off about 10 cc. of the solution, then diluting with water until lead iodide began to separate; now, on replacing the removed portion, the solution again became clear. In this way eight new crops of crystals were obtained. These were labeled I, J, K, L, M, N, O and P.

To the mother-liquors from each of these last was then added 50 cc. of absolute alcohol. Quite large crops of crystals were again obtained, and labeled I', J', K', L', M', N', O' and P'. The mother-liquors from these last were then evaporated to dryness.

Twenty-eight compounds had now been prepared from solutions containing varying quantities of lead bromide and potassium iodide. Furthermore, the proportion of water present had been varied, and finally a series obtained by the addition of alcohol. It was hoped that somewhere in this series of compounds the bromiodoplumbite would be found, but on carefully testing each one qualitatively, it was found that all of the compounds contained iodine, while not one of the twenty-eight showed the slightest trace of bromine. The residues obtained by evaporating the final mother-liquors to dryness showed the presence of both iodine and bromine. Evidently, only potassium iodo-plumbite had been formed in each case.

It has been shown[1] that most probably the only potassium iodoplumbite which can exist has the formula $KPbI_3.2H_2O$. To test again the correctness of this view, quantitative analyses were made of the compound B', prepared from a hot solution, and the compound X, prepared in the cold. In X, only water and lead were determined, the lead being converted directly into the sulphate by treatment with sulphuric acid. Complete analyses of B' were made according to the method described above.

I. 0.7634 gram of X lost 0.0401 gram of water and yielded 0.3513 gram of lead sulphate $= 0.2399$ gram of lead.

II. 0.5304 gram of X lost 0.0269 gram of water and yielded 0.2425 gram of lead sulphate $= 0.1656$ gram of lead.

	I.	II.	Calculated for $KPbI_3.2H_2O$.
H_2O	5.25	5.07	5.43 per cent.
Pb	31.43	31.22	31.23 "

I. 1.0329 grams of B' gave 0.0544 gram of H_2O.

    0.4698 gram of $PbSO_4 = 0.3208$ gram Pb.

    1.1023 grams of $AgI = 0.5956$ gram I.

    0.3965 gram of $K_2PbCl_6 = 0.0639$ gram K.

II. 1.0032 grams of B' gave 0.0531 gram of H_2O.

    0.4562 gram of $PbSO_4 = 0.3115$ gram Pb.

    1.0677 grams of $AgI = 0.5769$ gram I.

    0.3893 gram of $K_2PbCl_6 = 0.0627$ gram K.

	I.	II.	Calculated for $KPbI_3.2H_2O$.
H_2O	5.27	5.29	5.43 per cent.
Pb	31.06	31.05	31.23 "
I	57.66	57.51	57.43 "
K	6.19	6.25	5.91 "
	100.18	100.10	100.00 "

Solution of Lead Iodide in Potassium Bromide.

Preliminary Experiments.—Having obtained only potassium iodoplumbite, $KPbI_3.2H_2O$, on dissolving lead bromide in an aqueous solution of potassium iodide, it was decided to change the conditions of experiment and dissolve lead iodide in a solution of potassium bromide. To this end a solution of potassium bromide was prepared by dissolving 190 grams of potassium bromide in

[1] This Journal **14**, 107.

350 cc. of water. Three portions, 50 cc. each, of this solution, labeled respectively *A*, *B* and *C*, were heated almost to boiling. To *A* was added 20 grams of lead iodide. Solution was effected quite readily. On cooling, needle-shaped crystals separated in such large quantities that the mass became almost solid. The possibility of the presence of alkaline halide as an impurity was so great that it was decided not to analyse this compound. To *B* was added 10 grams of lead iodide, all dissolved, and, on cooling, crystals, similar in appearance to those in *A*, were formed, but not in such large quantity. The mother-liquor was pumped off and the crystals dried as before, and labeled *B*. To *C* was added 5 grams of lead iodide. No crystals formed in this solution, either after cooling or after standing several days.

To try the effect of using a more dilute solution of potassium bromide, three portions, 50 cc. each, of the solution used in the preceding experiments were labeled respectively *A'*, *B'* and *C'*. To each was added 50 cc. of water and all were then heated to boiling. To *A'* was added 20 grams of lead iodide, to *B'* 10 grams and to *C'* 5 grams. In the case of *A'*, only a portion of the lead iodide dissolved, even after continued boiling, so the mass was set aside without filtering. Soon, crystals of lead iodide began to form. After standing twenty-four hours there were found in the vessel the red crystals of lead iodide, white needles similar to *A* and *B* above, and a third substance having the appearance of black specks in the mass. On examination with the microscope these last were found to be distinct crystals, dark green in color. After standing several days all the crystals in the vessel changed to white needles. In *B'* all of the lead iodide dissolved, though quite slowly. On cooling, lead iodide first crystallised out of the solution. After standing twenty-four hours there were found, as in *A'*, crystals of lead iodide, white needles, and the tabular green crystals. The last were much better developed than in *A'*. No separation could be made for analysis. In *C'* the lead iodide dissolved quite readily. After standing twenty-four hours, only the green tabular crystals were found in the solution. These were dried and labeled *C'*. In form they resemble closely potassium bromoplumbite.[1]

The compounds *B* and *C'* showed, by qualitative tests, the presence of both iodine and bromine. An addition of water to the

[1] This Journal **14**, 124.

mother-liquor from *B* caused the separation of a large quantity of needle-shaped crystals. These were not analysed. An addition of alcohol to the mother-liquor from *C′* caused the separation of a flocculent white compound. This compound was dried and labeled *C″*.

1.1812 grams of *B* gave 1.2943 grams of AgI and AgBr. This was transformed into 0.8995 gram of AgCl, which gives in original substance 0.3123 gram of I and 0.3049 gram of Br.

0.6729 gram of *C′* gave 0.7325 gram of AgI and AgBr. This was transformed into 0.5320 gram of AgCl, which gives in original substance 0.0956 gram of I and 0.2365 gram of Br.

0.8470 gram of *C″* gave 0.9355 gram of AgI and AgBr. This was transformed into 0.6688 gram of AgCl, which gives in original substance 0.1601 gram of I and 0.2720 gram of Br.

	B.	*C′*.	*C″*.	Calculated for $PbI_2.KBr$.	$PbBr_2.KI$.
I	26.44	14.21	18.90	43.77	23.81 per cent.
Br	25.81	35.15	32.11	13.79	30.01 "

Series of Isomorphous Mixtures prepared by Dissolving Lead Iodide in an Aqueous Solution of Potassium Bromide.

Up to this point in the investigation, it has been shown that when lead bromide is dissolved in a somewhat concentrated solution of potassium iodide, only potassium iodoplumbite, $KPbI_3$. $2H_2O$, crystallises from the solution. On the other hand, it has been shown that when lead iodide is dissolved in solutions of potassium bromide of varying concentration, compounds are formed which show varying proportions of iodine and bromine. These proportions seem to vary according to the proportions of iodine and bromine in the solutions from which the salts crystallised. The composition of these compounds does not correspond to either of the simple formulas $KPbI_2Br$ ($PbI_2.KBr$) or $KPbIBr_2$ ($PbBr_2.KI$). These facts suggest that the compounds are isomorphous mixtures of potassium iodoplumbite and potassium bromoplumbite. To test this view, and, if correct, to determine what must be the composition of a solution from which a compound of a given composition is formed, the following experiments were made. All materials used in these experiments were kept in a warm closet at the uniform temperature of 29° C. The potassium-bromide solution used was made by dissolving 268 grams of the

salt in 400 cc. of water. 50 cc. of this solution contained 28.15 grams of potassium bromide and 41.85 grams of water.

Experiments with concentrated solutions of potassium bromide.—Three portions, 50 cc. each, of the potassium bromide solution mentioned above were heated almost to boiling. These were labeled A, B and C. To A was added 11 grams of lead iodide, to B 10 grams and to C 9 grams. The lead iodide dissolved in each case. The percentage composition of these hot solutions is given in the table below. After one hour, needle-shaped crystals began to form in A. Similar crystals began to form in B after two hours. Only after standing twenty-four hours did crystals begin to form in C. These crystals were similar to those in A and B. All three solutions were allowed to stand five days. The crystals were then dried and labeled respectively A, B and C. About 5 cc. of the mother-liquor from each was drawn off into a crucible and analysed. These portions were labeled respectively A', B' and C'. To the remainder of the mother-liquors water was added until the point of decomposition with setting free of lead iodide was almost reached. In this way to the mother-liquor from A was added 21 cc. of water; to that from B, 25 cc.; and finally, to that from C, 25 cc. White needle-shaped crystals began to separate immediately in each vessel. After standing six hours the crystals were dried and labeled A', B' and C'. A portion of the mother-liquor from each of these was analysed as before. These portions were labeled A'', B'' and C''. To the main portion of these mother-liquors was added absolute alcohol, until the point of decomposition of the solution was almost reached. In this way to the mother-liquor from the compound A' was added 12 cc. of absolute alcohol; to that from B', 13.5 cc., and to that from C', 18.5 cc. Large quantities of white, needle-shaped crystals again formed in each vessel. These were dried and labeled respectively A'', B'' and C''.

Analyses of Mother-liquors.

7.7897 grams of A' gave 3.8026 grams of H_2O.

0.4812 gram of $PbSO_4 = 0.3286$ gram of Pb.

5.8235 grams of AgI and AgBr. This was transformed into 4.3010 grams of AgCl, which gives in original solution 0.5069 gram I and 2.0792 grams Br.

6.5905 grams of $K_2PtCl_6 = 1.0617$ grams of K.

7.7016 grams of B' gave 3.8369 grams of H_2O.

0.4461 gram of $PbSO_4 = 0.3046$ gram of Pb.

5.6110 grams of AgI and AgBr. This was transformed into 4.1535 grams of AgCl, which gives in original solution 0.4555 gram of I and 2.0292 grams of Br.

6.4375 grams of $K_2PtCl_6 = 1.0371$ grams of K.

7.7520 grams C' gave 3.8091 grams of H_2O.

0.4863 gram of $PbSO_4 = 0.3321$ gram of Pb.

5.7705 grams of AgI and AgBr. This was transformed into 4.2775 grams of AgCl, which gives in original solution 0.4470 gram of I and 2.1038 grams of Br.

6.5545 grams of $K_2PtCl_6 = 1.0559$ grams of K.

6.4912 grams of A'' gave 4.3402 grams of H_2O.

0.1792 gram of $PbSO_4 = 0.1224$ gram of Pb.

3.2090 grams of AgI and AgBr. This was transformed into 2.3855 grams of AgCl, which gives in original solution 0.2242 gram of I and 1.1892 grams of Br.

3.7970 grams of $K_2PtCl_6 = 0.6117$ gram of K.

6.5163 grams of B'' gave 4.3277 grams of H_2O.

0.2200 gram of $PbSO_4 = 0.1502$ gram of Pb.

3.2390 grams of AgI and AgBr. This was transformed into 2.4075 grams of AgCl, which gives in original solution 0.2280 gram of I and 1.1989 grams of Br.

3.7770 grams of $K_2PtCl_6 = 0.6085$ gram of K.

6.5499 grams of C'' gave 4.3154 grams of H_2O.

0.2103 gram of $PbSO_4 = 0.1436$ gram of Pb.

3.3230 grams of AgI and AgBr. This was transformed into 2.4725 grams of AgCl, which gives in original solution 0.2242 gram of I and 1.2377 grams of Br.

3.9140 grams of $K_2PtCl_6 = 0.6305$ gram of K.

The figures under A, B and C in the table below represent the percentage composition of the solutions A, B and C mentioned above, and were calculated directly from the weights of water, potassium bromide and lead iodide used in making up the . solution.

From the hot solutions A, B and C crystals separated on cooling, but from the mother-liquors A', B', C', A'', B'' and C'' (see table below) crystals separated only after the addition of water and alcohol in the quantities already mentioned.

TABLE I.

	H₂O.	Pb.	I.	Br.	K.	Total.
A	51.67	6.10	7.48	23.33	11.42	100.00
B	52.31	5.61	6.89	23.63	11.56	100.00
C	52.98	5.11	6.28	23.92	11.71	100.00
A′	48.82	4.22	6.51	26.69	13.63	99.87
B′	49.82	3.96	5.91	26.35	13.47	99.51
C′	49.14	4.28	5.77	27.14	13.62	99.95
A″	66.86	1.89	3.45	18.32	9.42	99.94
B″	66.41	2.30	3.50	18.40	9.34	99.95
C″	65.88	2.19	3.42	18.90	9.63	100.02

Analyses of Compounds.

1.0012 grams of A gave 0.0313 gram of H_2O.

0.5320 gram of $PbSO_4 = 0.3633$ gram of Pb.

1.1073 grams AgI and AgBr. This was transformed into 0.7672 gram of AgCl, which gives in original substance 0.2756 gram of I and 0.2542 gram of Br.

0.4581 gram of $K_2PtCl_6 = 0.0738$ gram of K.

1.0015 grams of B gave 0.0315 gram of H_2O.

0.5343 gram of $PbSO_4 = 0.3649$ gram of Pb.

1.1058 grams AgI and AgBr. This was transformed into 0.7670 gram of AgCl, which gives in original substance 0.2727 gram of I and 0.2558 gram of Br.

0.4427 gram of $K_2PtCl_6 = 0.0713$ gram of K.

1.0058 grams of C gave 0.0313 gram of H_2O.

0.5374 gram of $PbSO_4 = 0.3670$ gram of Pb.

1.1133 grams of AgI and AgBr. This was transformed into 0.7726 gram of AgCl, which gives in original substance 0.2732 gram of I and 0.2586 gram of Br.

0.4560 gram of $K_2PtCl_6 = 0.0735$ gram of K.

1.0010 grams of $A′$ gave 0.0307 gram of H_2O.

0.5334 gram of $PbSO_4 = 0.3643$ gram of Pb.

1.1041 grams of AgI and AgBr. This was transformed into 0.7674 gram AgCl, which gives in original substance 0.2666 gram of I and 0.2599 gram of Br.

0.4361 gram of $K_2PtCl_6 = 0.0703$ gram of K.

0.9150 gram of $B′$ gave 0.0285 gram of H_2O.

0.4909 gram of $PbSO_4 = 0.3352$ gram of Pb.

1.0114 grams of AgI and AgBr. This was transformed into 0.7030 gram of AgCl, which gives in original substance 0.2440 gram of I and 0.2383 gram of Br.

0.4111 gram of $K_2PtCl_6 = 0.0662$ gram of K.

1.0075 grams of C' gave 0.0317 gram of H_2O.

0.5434 gram of $PbSO_4 = 0.3711$ gram of Pb.

1.1129 grams of AgI and AgBr. This was transformed into 0.7768 gram of AgCl, which gives in original substance 0.2568 gram of I and 0.2714 gram of Br.

0.4467 gram of $K_2PtCl_6 = 0.0720$ gram of K.

1.0017 grams of A'' gave 0.0314 gram of H_2O.

0.5409 gram of $PbSO_4 = 0.3694$ gram of Pb.

1.1072 grams of AgI and AgBr. This was transformed into 0.7752 gram of AgCl, which gives in original substance 0.2473 gram of I and 0.2764 gram of Br.

0.4449 gram of $K_2PtCl_6 = 0.0717$ gram of K.

1.0031 grams of B'' gave 0.0321 gram of H_2O.

0.5454 gram of $PbSO_4 = 0.3725$ gram of Pb.

1.1095 grams of AgI and AgBr. This was transformed into 0.7795 gram of AgCl, which gives in original substance 0.2384 gram of I and 0.2844 gram of Br.

0.4512 gram of $K_2PtCl = 0.0727$ gram of K.

1.0015 grams of C'' gave 0.0315 gram of H_2O.

0.5471 gram of $PbSO_4 = 0.3736$ gram of Pb.

1.1083 grams of AgI and AgBr. This was transformed into 0.7833 gram of AgCl, which gives in original substance 0.2214 gram of I and 0.2973 gram of Br.

0.4514 gram of $K_2PtCl_6 = 0.0727$ gram of K.

TABLE II.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	3.13	36.29	27.53	25.39	7.37	99.71
B	3.15	36.44	27.23	25.54	7.12	99.48
C	3.11	36.49	27.16	25.71	7.31	99.78
A'	3.07	36.39	26.63	25.96	7.02	99.07
B'	3.11	36.63	26.67	26.04	7.23	99.68
C'	3.15	36.83	25.49	26.94	7.15	99.56
A''	3.13	38.88	24.69	27.59	7.16	99.45
B''	3.20	37.13	23.77	28.35	7.25	99.70
C''	3.15	37.30	22.11	29.69	7.26	99.51

Experiments with dilute solutions of potassium bromide.—Three portions, 50 cc. each, of the potassium bromide solution, labeled D, E and F, were heated almost to boiling.

To D was added 6 grams of lead iodide, to E 5 grams, and to F 4 grams. The lead iodide dissolved in each case. The percentage composition of these solutions is as follows:

TABLE III.

	H_2O.	Pb.	I.	Br.	K.	Total.
D	72.85	2.15	2.62	15.03	7.35	100.00
E	73.44	1.80	2.21	15.14	7.41	100.00
F	74.03	1.45	1.78	15.27	7.47	100.00

After standing one hour and a half, small, olive-green crystals began to form in D. These crystals are generally tabular; sometimes they have the appearance of four-rayed stars. After three hours, crystals similar to those in D began to form in E. Only after standing two days did a few small tabular crystals form in F. All three solutions were allowed to stand five days. At the end of this time the crystals in D and E had grown somewhat larger, while those in F had passed back into solution. The crystals from D and E were dried and labeled D and E. A close inspection of the crystals D showed a few white needles beginning to form on the edges of some of the tabular crystals. Such as these were discarded.

It was impossible to obtain any satisfactory crystals by dilution of the solution F or the mother-liquors from D and E, owing to the ready separation of lead iodide.

Analyses of Compounds.

1.0004 grams of D gave 0.6576 gram of $PbSO_4 = 0.4491$ gram of Pb.

1.0922 grams of AgI and AgBr. This was transformed into 0.7839 gram AgCl, which gives in original substance 0.1762 gram I and 0.3260 gram of Br.

0.2831 gram of $K_2PtCl_6 = 0.0456$ gram of K.

0.9993 gram of E gave 0.6647 gram $PbSO_4 = 0.4539$ gram of Pb.

1.0917 grams AgI and AgBr. This was transformed into 0.7910 gram AgCl, which gives in original substance 0.1493 gram of I and 0.3470 gram of Br.

0.2791 gram of $K_2PtCl_6 = 0.0450$ gram of K.

TABLE IV.

	Pb.	I.	Br.	K.	Total.
D	44.89	17.61	32.59	4.56	99.65
E	45.42	14.94	34.72	4.50	99.58

Explanation of Analytical Results.

Composition of the needle-shaped crystals.—At the beginning of the investigation it was hoped salts such as $KPbI_2Br.xH_2O$ and $KPbIBr_2.xH_2O$ might be obtained. The calculated composition of these salts, assuming only one molecule of water of crystallisation to be present, is as follows :

	H_2O.	Pb.	I.	Br.	K.
$KPbI_2Br.H_2O$	3.01	34.62	42.45	13.38	6.54 per cent.
$KPbIBr_2.H_2O$	3.27	37.57	23.03	29.03	7.10 "

All of the compounds prepared from concentrated solutions of potassium bromide are well formed, needle-shaped crystals, but they show variations in composition (see Table II), corresponding in a general way to the variations in the composition of the solutions from which they crystallised. This suggests that these compounds are isomorphous mixtures of the simple iodoplumbite and bromoplumbite. This view is rendered more probable by the fact that in the above series the percentages of lead and bromine increase, while that of iodine decreases. This increase in the amount of lead is to be expected, as there is 42.58 per cent. of lead in the salt $KPbBr_3$, and only 33.02 per cent. of lead in the salt $KPbI_3$.

Since the composition of the simple halo-plumbites corresponds to the formulæ $KPbI_3.2H_2O$[1] and $KPbBr_3.H_2O$,[2] it seemed reasonable to expect that the isomorphous mixtures should be made up of varying proportions of these two substances. As will be seen by the calculations below this is true, with the exception that the iodoplumbite has only 1 molecule of water of crystallisation.

The composition of the salts $KPbI_3.2H_2O$ and $KPbBr_3.H_2O$ is as follows :

	H_2O.	Pb.	I.	Br.	K.
$KPbI_3.2H_2O$	5.43	31.23	57.43	...	5.91 per cent.
$KPbBr_3.H_2O$	3.57	41.06	...	47.61	7.76 "

Taking now the case of the compound *C* (Table II), the analytical error being least here, and assuming that this is an isomor-

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[1] This Journal **14**, 110.   [2] *Ibid.* 124.

phous mixture of $KPbI_3.2H_2O$ and $KPbBr_3.H_2O$, then the 27.16 per cent. of iodine, present as iodoplumbite, would require 2.57 per cent. of water, for in the salt $KPbI_3.2H_2O$ there is present 57.43 per cent. of iodine and 5.43 per cent. of water.

$$57.43 : 5.43 :: 27.16 : x = 2.57 \text{ per cent. of water.}$$

Similarly, the 25.71 per cent. of bromine would require 1.93 per cent. of water, for the salt $KPbBr_3.H_2O$ contains 47.61 per cent. of bromine and 3.57 per cent. of water.

$$47.61 : 3.57 :: 25.71 : x = 1.93 \text{ per cent. of water.}$$

The sum of these amounts of water, required on the above assumption, is 4.50 per cent. $(2.57 + 1.93)$; but by analysis there was found only 3.11 per cent. of water.

Evidently the compound does not contain the common iodoplumbite $KPbI_3.2H_2O$ and bromoplumbite $KPbBr_3.H_2O$. This same calculation proves that the mixture cannot be $KPbI_3.2H_2O$ and $KPbBr_3$, for the 27.16 per cent. of iodine requires only 2.57 per cent. of water, if the iodine is present as $KPbI_3.2H_2O$, while there was actually found 3.11 per cent. Assuming now that the mixture is composed of $KPbI_3$ and $KPb_3.2H_2O$, then the 25.71 per cent. bromine in *C* would require 3.85 per cent. of water, for the salt $KPbBr_3.2H_2O$ contains 45.97 per cent. of bromine and 6.88 per cent. of water.

$$45.97 : 6.88 :: 25.71 : x = 3.85 \text{ per cent. of water.}$$

Plainly this is wrong. The assumption that the mixture is $KPbI_3$ and $KPbBr_3.H_2O$ is also false; for the 25.71 per cent. of bromine requires, according to this formula, only 1.93 per cent. of water, since the salt $KPbBr_3.H_2O$ contains 47.61 per cent. of bromine and 3.57 per cent. of water.

$$47.61 : 3.57 :: 25.71 : x = 1.93 \text{ per cent. of water.}$$

Finally, assume that the mixture is composed of the salts $KPbI_3.H_2O$ and $KPbBr_3.H_2O$. The composition of these salts is as follows:

	H_2O.	Pb.	I.	Br.	K.	
$KPbI_3.H_2O$	2.79	32.10	59.04	...	6.07	per cent.
$KPbBr_3.H_2O$	3.57	41.06	...	47.61	7.76	"

Now, the 27.16 per cent. of iodine found in *C* would require 1.28 per cent. of water, and the 25.71 per cent. of bromine would require 1.93 per cent. of water, giving thus the total amount of water as 3.21 per cent., whereas there was actually found 3.11 per

cent. Continuing now the same method of calculation for lead and potassium as was made use of in the case of water, it is found that 27.16 per cent. of iodine requires 14.77 per cent. of lead, and 25.71 per cent. of bromine requires 22.17 per cent. of lead, giving a total of 36.94 per cent. There was found 36.49 per cent.

As to potassium, 27.16 per cent. of iodine requires 2.79 per cent. of potassium, and 25.71 per cent. of bromine requires 4.19 per cent. of potassium, giving a total of 6.98 per cent. There was found 7.31 per cent.

It will be noticed that, according to the above calculations, the quantity of lead found by analysis is 0.45 per cent. less than that required by calculation, and that the potassium found by analysis is 0.33 per cent. greater than that required by calculation. This is probably to be partially accounted for by experimental error: on the other hand, this variation is rather to be expected if the method of preparation of the salt be taken into consideration. On account of its ready decomposition by water the compound could not be washed free from the mother-liquor, but was dried as quickly as possible, by means of a filter-pump* and pressing between folds of drying-paper. Very probably, therefore, a small amount of alkali halide from the mother-liquor remained on the surface of the crystals. If this be true, then the calculated results for lead should be higher than the amounts found by analysis, while the calculations for potassium should be low, for, according to the above calculations, the entire amount of each halide has been considered in the form of a halo-plumbite.

Taking all of the above facts into consideration, it seems most probable that the needle-shaped crystals are isomorphous mixtures of the two salts $KPbI_3.H_2O$ and $KPbBr_3.H_2O$.

Composition of the tabular crystals.—The compounds D and E (Table IV) show by their percentage composition that they cannot be isomorphous mixtures of the salts $KPbI_3.H_2O$ and $KPbBr_3.H_2O$. In the first place, they contain no water of crystallisation. The salt $KPbI_3$ contains 33.02 per cent. of lead, while the salt $KPbBr_3$ contains 42.58 per cent. of lead. In any isomorphous mixture of these two salts the percentage of lead must vary between the extremes 33.02 and 42.58. Therefore, as in D there is present 44.89 per cent. of lead, and in E 45.42 per cent., this explanation of the composition of the compounds is plainly wrong.

The large percentage of lead found suggests the possibility of the presence of free lead bromide or iodide. Assuming that in D there is present $KPbBr_3$ and PbI_2, then the 32.59 per cent. of bromine would require 28.11 per cent. lead, and the 17.61 per cent. of iodine would require 14.36 per cent. of lead, giving the total percentage of lead required by this hypothesis 42.47 per cent., whereas there was actually found 44.89 per cent. Furthermore, the 32.59 per cent. of bromine would require 5.31 per cent. of potassium, but there was found only 4.56 per cent. This hypothesis must therefore be discarded. Again, assuming that the crystals are composed of $KPbI_3$ and $PbBr_2$, then the 17.61 per cent. of iodine would require 1.81 per cent. of potassium. As 4.56 per cent. was found, this view is wrong.

The large percentage of lead suggests two other possible explanations of the composition of the tabular crystals, namely, a mixture of $KPbI_3$, $KPbBr_3$ and PbI_2 or a mixture of $KPbI_2$, $KPbBr_3$ and $PbBr_2$. The first of these has already been shown to be false, for if all of the bromine is present as bromoplumbite, then the 32.59 per cent. of bromine in D would require 5.31 per cent. of potassium, which is greater than the amount of potassium found, 4.56 per cent., and, according to this view, still more potassium should be present in the form of iodoplumbite. This leaves, as the only other explanation, the idea that the tabular crystals are composed of $KPbI_3$, $KPbBr_3$ and $PbBr_2$. Assume, now, that this is correct. In the compound D, the 17.61 per cent. of iodine, present as iodoplumbite, would require 9.57 per cent. of lead and 1.81 per cent. of potassium. Deducting these amounts from the total amounts found by analysis, there remains 2.75 per cent. of potassium as bromoplumbite, and 35.32 per cent. of lead as bromoplumbite and lead bromide. The 2.75 per cent. of potassium present as bromoplumbite requires 16.87 per cent. of bromine and 14.55 per cent. of lead. Deducting the 16.87 per cent. of bromine from the total amount of bromine, there is left 15.72 per cent. of bromine as lead bromide, and deducting the 14.55 per cent. of lead from the 35.32 per cent. of lead present as bromoplumbite and lead bromide, there remains 20.77 per cent. of lead as lead bromide. Now, lead bromide contains 56.40 per cent. of lead and 43.60 per cent. bromine. Therefore the 20.77 per cent. of lead would require, to form lead bromide, 16.06 per cent. of bromine. By the above calculation there was found 15.72 per cent. of bromine.

The fact that in this last calculation, after deducting those amounts of the mixture present as potassium iodoplumbite and potassium bromoplumbite, the remaining lead and bromine are in the proportions necessary to form lead bromide, suggests the possibility that these tabular crystals are composed of $KPbI_3$ and KPb_2Br_5 ($2PbBr_2.KBr$). Now, KPb_2Br_5 is composed of 48.53 per cent. of lead, 46.88 per cent. of bromine and 4.59 per cent. of potassium. Accordingly, the 35.32 per cent. of lead remaining in *D*, after deducting the amount present as iodoplumbite, would require 34.12 per cent. of bromine and 3.34 per cent. of potassium, but there was found by analysis only 32.59 per cent. of bromine, and, after deducting from the total amount of potassium, 4.56 per cent., that present as iodoplumbite, 1.81 per cent., there remains only 2.75 per cent. of potassium. That this hypothesis is wrong can best be shown by another form of calculation. Assume that in these crystals all bromine is present as KPb_2Br_5, which for purposes of calculation can be written ($KPbBr_3.PbBr_2$). Then in that method of calculation based upon the assumption that these crystals are composed of $KPbI_3$, $KPbBr_3$ and $PbBr_2$, the ratio between the calculated amounts of $KPbBr_3$ and $PbBr_2$ should be a constant. This constant is that expressing the ratio between the molecular weights of $KPbBr_3$, 484.7, and $PbBr_2$, 356.91, and its numerical value is 0.7549. Now, *D* contains 34.17 per cent. of $KPbBr_3$ and 36.49 per cent. of $PbBr_2$. The ratio here is 1.0679, instead of 0.7549, as required by the hypothesis. By similar calculations the ratio in the salt *E* (Table II) is 1.0328. Another compound, tabular in form, has been prepared which shows a ratio of 1.3579.

From all of the above calculations it seems fair to conclude that the tabular crystals are mixtures of varying proportions of potassium iodoplumbite, $KPbI_3$, potassium bromoplumbite, $KPbBr_3$, and lead bromide, $PbBr_2$.

Compounds formed from Solutions containing Increasing Quantities of Iodine and Decreasing Quantities of Bromine.

As it had been found in the first part of the investigation (see section "Solution of Lead Bromide in Potassium Iodide") that when iodine is largely in excess of bromine only the iodoplumbite crystallised from the solution, the investigation was then directed

towards the determination of the point at which the bromoplumbite ceased to crystallise from the solution.

21.34 grams of potassium bromide and 8.3628 grams of potassium iodide were dissolved in 40.95 grams of water. To this solution was added 8 grams of lead iodide, and the mass heated to boiling in a flask connected with an inverted condenser. After cooling slightly the solution was filtered from the small amount of insoluble substance remaining, and on further cooling needle-shaped crystals separated in large quantity. These were dried and labeled *A*. Qualitative tests showed the presence of both iodine and bromine in this compound.

Another compound, *B*, similar in appearance to *A*, was prepared by dissolving 9 grams of lead iodide in a solution of 15.34 grams of potassium bromide and 16.7256 grams of potassium iodide in 40.95 grams of water. This compound showed by qualitative test a large amount of iodine, but only a small quantity of bromine.

Finally, a third compound, *C*, similar to *A* and *B*, was prepared by dissolving 9 grams of lead iodide in a solution of 12.34 grams of potassium bromide and 20.907 grams of potassium iodide in 40.95 grams of water. This compound showed by qualitative tests the presence of a great quantity of iodine, but only a trace of bromine. So great was the quantity of crystals formed here that the mass became almost solid.

Analyses of Compounds.

1.0011 grams of *A* gave 0.0555 gram of H_2O.

0.4705 gram of $PbSO_4 = 0.3213$ gram of Pb.

1.0668 grams of AgI and AgBr. This was transformed into 0.6774 gram of AgCl, which gives in original substance 0.4847 gram of I and 0.0722 gram of Br.

0.4014 gram of $K_2PtCl_6 = 0.0647$ gram of K.

1.0027 grams of *B* gave 0.0551 gram of H_2O.

0.4621 gram of $PbSO_4 = 0.3156$ gram of Pb.

1.0656 grams of AgI and AgBr. This was transformed into 0.6636 gram of AgCl, which gives in original substance 0.5304 gram of I and 0.0357 gram of Br.

0.3861 gram of $K_2PtCl_6 = 0.0622$ gram of K.

1.0020 grams of *C* gave 0.0543 gram of H_2O.

0.4571 gram of $PbSO_4 = 0.3122$ gram of Pb.

1.0642 grams of AgI and AgBr. This was transformed into 0.6585 gram of AgCl, which gives in original substance 0.5445 gram of I and 0.0240 gram of Br.

0.3934 gram of $K_2PtCl_6 = 0.0634$ gram of K.

TABLE V.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	5.54	32.09	48.42	7.21	6.46	99.72
B	5.50	31.48	52.90	3.56	6·20	99.64
C	5.42	31.16	54.34	2.40	6.33	99.65

From these results it is evident that the point at which the iodoplumbite alone separates from the solution has almost been reached. The investigation was not carried further in this direction, because it has already been shown that if the ratio of iodine to bromine be sufficiently large, only the iodoplumbite is formed.

Furthermore, it was deemed unsafe to extend the experiments using the same weights of water, lead and potassium, for, even in *C*, so great a quantity of crystals formed, and there was consequently so great a concentration of the solution by water being taken up as water of crystallisation, that alkaline halide crystallised from the solution along with the needles. This is shown, in Table V, by the increase in the percentage of potassium in *C* over that in *B*. If no free potassium iodide or bromide had been present the percentage would have been less in *C* than in *B*.

From an examination of the percentages of water in Table V, it is seen that when the iodoplumbite is present in the mixture in much larger quantity than the bromoplumbite, the compound no longer has one molecule of water of crystallisation, but two molecules.

Compounds formed from Solutions containing Decreasing Quantities of Iodine and Increasing Quantities of Bromine.

In this series of experiments the same weights of potassium bromide were dissolved in constant quantities of water, but gradually increasing quantities of the lead iodide used in the first experiment were replaced by equivalent quantities of lead bromide, consequently the proportions of iodine and bromine alone varied.

A. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water. After heating nearly to boiling, 9 grams of lead

iodide was added. From this solution needle-shaped crystals separated. These were dried and labeled *A*.

B. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water, and, after heating, 5.00 grams of lead iodide and 3.1854 grams of lead bromide were added. On cooling, crystals similar to *A* separated from the solution. These were dried and labeled *B*.

Analyses of Compounds.

1.0005 grams of *A* gave 0.0320 gram of H_2O.

0.5363 gram of $PbSO_4 = 0.3662$ gram of Pb.

1.1037 grams of AgI and AgBr. This was transformed into 0.7680 gram of AgCl, which gives in original substance 0.2633 gram of I and 0.2623 gram of Br.

0.4466 gram of $K_2PtCl_6 = 0.0719$ gram of K.

1.0021 grams of *B* gave 0.0333 gram of H_2O.

0.5542 gram of $PbSO_4 = 0.3785$ gram of Pb.

1.1078 grams of AgI and AgBr. This was transformed into 0.7919 gram of AgCl, which gives in original substance 0.1894 grams of I and 0.3223 gram of Br.

0.4675 gram of $K_2PtCl_6 = 0.0753$ gram of K.

Table VI.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	3.20	36.60	26.32	26.22	7.19	99.53
B	3.32	37.77	18.90	32.16	7.51	99.66

From these figures it is readily seen that *B* contains much more bromoplumbite than does *A*.

C. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water. To the hot solution was added 3.00 grams of lead iodide and 4.7781 grams of lead bromide. Needle-shaped crystals again separated in small bundles resembling chestnut-burrs. These crystals were not analysed quantitatively, but showed by qualitative tests the presence of both iodine and bromine.

D. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water. This solution was heated to boiling, and 2.00 grams of lead iodide and 5.5745 grams of lead bromide added. On cooling, white lath-shaped crystals separated. On treating these crystals with water they become yellow, showing still the presence of iodoplumbite in the compound.

E. Finally, 27.35 grams of potassium bromide were dissolved in 40.95 grams of water, and, after heating, 0.5 gram of lead iodide and 6.769 grams of lead bromide added. On cooling, crystals separated. These crystals were transparent, and resembled somewhat crystals of potassium bromide. After thorough drying, one of these transparent crystals was placed in a drop of water, and with the aid of a magnifying glass it was seen to become opaque as soon as the water came in contact with it. The crystal failed to dissolve, even after long standing. This was evidently a double salt, or rather a mixture of two, for qualitative tests show the presence of a slight quantity of iodine and large quantities of bromine. Thus it is seen that iodine, even when present in the solution in slightest quantities, makes up part of the compound which crystallises from the solution ; differing thus from bromine in the presence of large proportions of iodine.

Further Proof of the Presence of Free Lead Bromide in the Tabular Crystals.

In the preceding section it has been shown that the iodoplumbite has a much greater tendency to form and separate from the solution than the bromoplumbite. It is probable, therefore, that when lead iodide is dissolved in a concentrated solution of potassium bromide, the first change which takes place is an exchange of bromine and iodine between part of the lead and part of the potassium. This is continued until equilibrium is established in that portion of the solution consisting of iodoplumbite and potassium iodide. As a result of this, there now remains in the rest of the mass a smaller quantity of potassium bromide and some lead bromide. Equilibrium is now established in this part of the solution. On cooling, the compound which crystallises contains, therefore, the excess of iodoplumbite and bromoplumbite held in solution by potassium iodide and potassium bromide, respectively.

It has been shown[1] that lead bromide is much less soluble in potassium bromide than is lead iodide in potassium iodide solution. Furthermore, all of the experiments on this subject show that the lead halides are much less soluble in dilute than in concentrated solutions of potassium halides. From these facts it is rather to be expected that when lead iodide is dissolved in a dilute solution of potassium bromide, the lead bromide formed in the

[1] This Journal **14**, 126.

exchange of halogens is more than sufficient to establish equilibrium with this dilute solution of potassium bromide. Consequently, on cooling, the excess of lead bromide would separate from the solution along with the iodoplumbite and bromoplumbite. If this be true, then the presence of a slightly larger quantity of potassium bromide in the solution should prevent the separation of free lead bromide, and only needle-shaped crystals, which have been shown to be mixtures of iodoplumbite and bromoplumbite, should crystallise from the solution. The following experiments seem to confirm this reasoning :

27.35 grams of potassium bromide was dissolved in 67.88 grams of water. After heating, 9 grams of lead iodide was dissolved in the solution. On cooling, tabular crystals separated.

0.9993 gram of this compound gave 0.6419 gram of $PbSO_4 =$ 0.4384 gram of Pb.

1.0922 grams of AgI and AgBr. This was transformed into 0.7710 gram of AgCl, which gives in original substance 0.2218 gram of I and 0.2901 gram of Br.

0.2752 gram of $K_2PtCl_6 = 0.0443$ gram of K.

<table>
<tr><td></td><td colspan="2">By Calculation.</td></tr>
<tr><td>Pb = 43.87 per cent.</td><td>$KPbI_3$ = 36.55 per cent.</td></tr>
<tr><td>I = 22.20   "</td><td>$KPbBr_3$ = 26.71   "</td></tr>
<tr><td>Br = 29.03   "</td><td>$PbBr_2$ = 36.27   "</td></tr>
<tr><td>K = 4.43   "</td><td></td></tr>
<tr><td>Total = 99.53   "</td><td>Total = 99.53   "</td></tr>
</table>

Now, using the same quantities of water and lead iodide as used in the above experiment, but increasing the weight of potassium bromide from 27.35 grams to 32.35 grams, solution was effected by heating. From this solution, on cooling, only needle-shaped crystals separated, confirming thus the views expressed above. Here the solution was concentrated by the addition of potassium bromide.

This could also be effected by using a smaller quantity of water for the solution of the 27.35 grams of potassium bromide used in the first experiment. These conditions have already been complied with (Experiment *A*, p. 101) and only needle-shaped crystals obtained. The analysis of these needles shows them to be composed of only potassium iodoplumbite and potassium bromoplumbite.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.[1]

IV.—THE ACTION OF ETHYL ALCOHOL ON PARADIAZOTOL-UENESULPHONIC ACID UNDER DIFFERENT PRESSURES.

By Ira Remsen and Paul J. Dashiell.

In the first article[2] in this series it was shown that the nature of the reaction that takes place when ethyl alcohol and paradiazo-toluenesulphonic acid are heated together varies with the pressure. Experiments were made under pressures from 90 mm. to 500 mm. of mercury, and the following paragraph, quoted from the article referred to, sums up the results reached: "The experiments above described show that the higher the pressure the larger the proportion of ethoxy compound formed, and the lower the pressure the larger the proportion of toluenesulphonic acid formed."

"Under high pressure the reaction takes place as represented in this equation:

$$C_6H_3 \begin{cases} CH_3 \\ SO_3 \\ N_2 \end{cases} > + \, C_2H_5OH = C_6H_3 \begin{cases} CH_3 \\ SO_3H \\ OC_2H_5 \end{cases} + N_2.$$
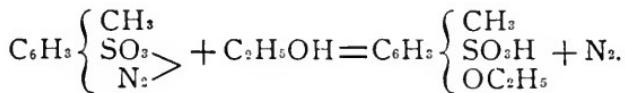
While at low pressure it takes place according to this equation:

$$C_6H_3 \begin{cases} CH_3 \\ SO_3 \\ N_2 \end{cases} > + C_2H_5OH = C_6H_4 < \begin{matrix} CH_3 \\ SO_3H \end{matrix} + N_2 + C_2H_4O."$$
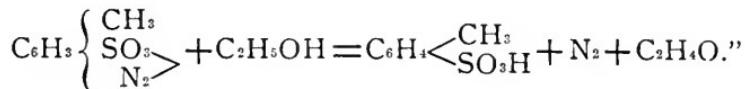
Although the conclusions stated were undoubtedly justified, still the work was not very satisfactory as regards the details, and it seemed desirable to study the reactions more thoroughly, in the hope that the effect of the pressure on the course of the reaction might be followed more closely. We were fortunate enough to find a fairly satisfactory method of separating the products of the reactions, and thus of determining the relative quantity of each formed under different conditions. While the effect of change of pressure was the main point that we kept in view, the effect of the addition of water to the alcohol in various proportions was also studied.

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[1] For the articles I, II, and III, see This Journal **8**, 243; **9**, 387, and **11**, 319.
[2] *Loc. cit.* **8**, 243.

The diazo compound used was prepared by us starting with paranitrotoluene. There is no difficulty if the methods described by Beilstein and Kuhlberg[1] for the nitrotoluenesulphonic acid, of Brackett and Hayes[2] for the amidotoluenesulphonic acid, and of De Roode[3] for the diazo compound are followed.
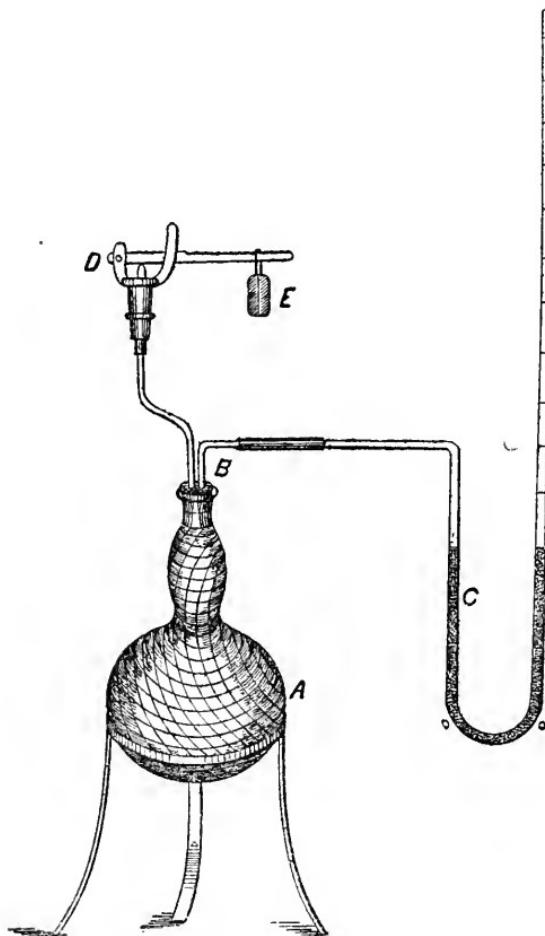
Apparatus.—The apparatus used in the experiments is that shown in the figure. It consists of the following parts: A strong balloon flask (A) of $1\frac{1}{2}$ litres capacity is covered with a close network of copper wire. The flask is fitted with a two-hole rubber stopper, which is bound down by wire during the experiment. Into one of the holes is fitted a bent glass tube (B)

[1] Annalen der Chemie **155**, 8.   [2] This Journal **9**, 399.   [3] *Ibid.* **13**, 219.

connecting with an open end U-tube mercury manometer, gradu-
ated in millimeters.   Into the other hole through the stopper is
fitted a copper tube, at the top of which is a conical valve pro-
vided with a lever, on which is hung a leaden weight.   By
adjusting this weight properly and keeping up a gentle heat, the
contents of the flask can be kept boiling at any desired pressure,
until the reaction is finished, the variations of the manometer not
exceeding five to ten millimeters.   In decomposing at high pres-
sures, the precaution was taken to heat rapidly and thus raise the
pressure to the desired point as quickly as possible, for the
purpose of avoiding the reactions at lower pressures.

Method of Separating the Two Products.

After the decomposition of the diazo compound with alcohol,
there are two products in solution in the excess of alcohol, viz.,
orthotoluenesulphonic acid and ethoxytoluenesulphonic acid. After
evaporating off the alcohol, the residue was dissolved in water and
neutralised with barium carbonate.   The filtered solution of the
two barium salts was then evaporated to dryness on the water-
bath.   It was found that the ethoxy barium salt is but slightly
soluble in cold 94-per cent. alcohol, and far more soluble at the
boiling-point, while the salt of orthotoluenesulphonic acid is but
little soluble in boiling alcohol.   Upon these facts the following
method of separation rests.   To the united portions of the barium
salts a convenient quantity of alcohol was added, and the temper-
ature raised to boiling for a few minutes.   The solid matter was
allowed to settle, the solution decanted into a beaker, and the pro-
cess repeated.   The decanted portions were raised to boiling and
passed through a weighed filter.   The residue in the flask was
then boiled with a third portion of alcohol, and thrown on the
same filter.   These repeated partial extractions were necessary on
account of the ready deposition of the ethoxy salt on slight cool-
ing of its solution in alcohol.   The filtrate was evaporated to dry-
ness on the water-bath.   The residue was dried at 100° C. in the
air-bath.   A determination of barium was made in each product.

As an example of the results obtained the following is given :

Weight of barium salts,		9.1 grams.
[A] Weight of portion extracted by alcohol,	3.6	
[B] Weight of residue,		5.3

Analysis of [A].—0.2188 gram of anhydrous salt gave 0.0913 gram of barium sulphate.

$$\text{Calculated for } C_6H_3{\overset{/CH_3}{\underset{\backslash O.C_2H_5}{-SO_3ba.}}}$$

	Calculated for C_6H_3—SO_3ba.	Found.
Ba	24.16	24.49

Analysis of [B].—0.2332 gram of anhydrous salt gave 0.1129 gram of barium sulphate.

$$\text{Calculated for } C_6H_4{\overset{\diagup CH_3}{-SO_3ba.}}$$

	Calculated for C_6H_4—SO_3ba.	Found.
Ba	28.60	28.42

The method of separation is quite good, as shown by the results of more than forty experiments. Moreover, the transformation of the two products of separation into derivatives of ethoxytoluene-sulphonic acid on the one hand, and of toluenesulphonic acid on the other, furnished direct evidence of its efficacy. A constant check was kept on the general results obtained by extraction, by analyses of the products.

As a point of interest in this connection, the exact solubilities of the two barium salts were determined. The crude products were recrystallised until their analyses showed them to be pure. The apparatus used in the determinations of solubility was constructed after the manner of that described by Victor Meyer.[1] Three experiments were made for the purpose of determining the solubility of each salt in alcohol at the boiling-point. The mean results showed that—

100 grams of 94-per cent. alcohol dissolve 0.230 gram of barium orthotoluenesulphonate.

100 grams of 94-per cent. alcohol dissolve 5.5 grams of barium para-ethoxyorthotoluenesulphonate.

The latter is, therefore, more than twenty times more soluble than the former.

Method of Work.

In the work to be described, a series of three experiments was made under each particular set of conditions under investigation. The exact method of procedure was as follows: A weighed quantity of the diazo compound (about 10 grams) was introduced into the dry flask together with 200 cc. of alcohol, and boiled under the conditions of pressure desired. The decomposition being complete, the contents of the flask were washed with alcohol

[1] Ber. d. chem. Ges. **8**, 998.

through a weighed filter, and the small quantity of undiazotised toluidinesulphonic acid (usually less than half a gram) dried and weighed. The figures given as representing the diazo compound in each case were obtained by subtracting this weight from the total introduced into the flask.

From the more or less colored filtrate the excess of alcohol was distilled off, leaving a dark, viscous mass. This was taken up in water, converted into the barium salts, the solution evaporated to dryness on the water-bath, and the two products separated as described above. In nearly all cases the quantity of alcohol used in the extraction was 250 cc. Care was taken to boil for the same length of time in the different experiments, and other precautions observed, in order that the results should be strictly comparable. In some cases this quantity of alcohol was insufficient for the solution of all the ethoxy salt, and more was used. In others it was excessive, but mention will be made of these points when the experiments are described. In each series of experiments, analyses were made of the separated products. In case the relative weights of the latter were found to be nearly the same for the three experiments in any series, analyses were made in but one case. If discrepancies occurred greater than might have been expected from the comparatively rough method of separation used, examinations of the products were made in each case. These analyses furnished means of judging how far the separation had been successful, and in some cases were used as a basis for correcting the figures representing the products isolated.

I.—Decomposition of the Diazo Compound at Constant Pressure, the Strength of Alcohol being Varied.

The pressure throughout these experiments was kept constant at 300 mm.

Experiments with Absolute Alcohol.—I. 9.5 grams of the diazo body were decomposed in 200 cc. of absolute alcohol. The odor of aldehyde was marked. The action continued about half an hour. The color of the solution passed through yellow to dull red. The barium salts showed a yellowish color in solution, but were free from color when dry.

Weight of barium salts,	12.15 grams.
[A] Weight of portion dissolved by alcohol,	5.10
[B] Weight of residue,	6.86

Analysis of [A].—0.2106 gram of anhydrous salt gave 0.0869 gram of barium sulphate.

$$\text{Calculated for } C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown O.C_2H_5}{-SO_3ba.}}}$$

	Calculated	Found.
Ba	24.16	24.17

Analysis of [B].—0.2348 gram of anhydrous salt gave 0.1133 gram of barium sulphate.

$$\text{Calculated for } C_6H_4{<}{\overset{CH_5}{\underset{SO_3ba}{}}}.$$

	Calculated	Found.
Ba	28.60	28.32

II. 10 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as in the last experiment.

Weight of barium salts,	12.21 grams.
Weight of portion dissolved by alcohol,	4.80
Weight of residue,	7.31

III. 8.9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. Same phenomena as before.

Weight of barium salts,	11.28 grams.
Weight of portion dissolved by alcohol,	5.45
Weight of residue,	5.72

If an average be taken of the figures representing the three portions of the ethoxy compound and compared with that for the hydrogen products, we find that they stand in the relation of 5.08 to 6.63. Representing the sum of these as one hundred, the ethoxy body is found to constitute 43.4 per cent. It appears from these experiments that in decomposition of the diazo body at 300 mm. pressure, both hydrogen and ethoxy reactions take place, the former to the greater extent. The results obtained by Remsen and Palmer[1] led them to the conclusion that the ethoxy reaction is the principal one under these conditions.

It will be noticed in these experiments, as in other series, that the results are not closely concordant. The general tendency as indicated by the averages taken is, however, unmistakable, as will be seen later.

Experiments with 95-per cent. Alcohol.—I. 9.4 grams of diazo compound were decomposed in 200 cc. of 95-per cent. alcohol.

[1] Loc. cit.

The odor of aldehyde was strong. The reaction required about twenty minutes. The solution during and after the reaction showed deeper color than in cases where absolute alcohol was used. The barium salts dried showed faint yellow color.

Weight of barium salts, 12.02 grams.
[A] Weight of portion dissolved by alcohol, 4.45
[B] Weight of residue, 7.45

Analysis of [A].—0.2684 gram of anhydrous salt gave 0.1104 gram of barium sulphate.

Calculated for $C_6H_3{-}SO_3ba{<}{\overset{CH_3}{O.C_2H_5}}$.

		Found.
Ba	24.16	24.14

Analysis of [B].—0.2533 gram of anhydrous salt gave 0.1215 gram of barium sulphate.

Calculated for $C_6H_4{<}{\overset{CH_3}{SO_3ba}}$.

		Found.
Ba	28.60	28.14

II. 9.7 grams of diazo compound were decomposed in 200 cc. of 95-per cent. alcohol. The same points were noticed as in the last experiment.

Weight of barium salts, 12.02 grams.
[A] Weight of portion dissolved by alcohol, 4.30
[B] Weight of residue, 7.60

Analysis of [A].—0.2664 gram of anhydrous salt gave 0.1179 gram of barium sulphate.

Calculated for $C_6H_3{-}SO_3ba{<}{\overset{CH_3}{O.C_2H_5}}$.

		Found.
Ba	24.16	24.63

Analysis of [B].—0.2444 gram of anhydrous salt gave 0.1179 gram of barium sulphate.

Calculated for $C_6H_4{<}{\overset{CH_3}{SO_3ba}}$.

		Found.
Ba	28.60	28.65

These results indicate a fair separation.

III. 8.75 grams of diazo compound were decomposed in 200 cc. of 95-per cent. alcohol.

Weight of barium salts, 10.49 grams.
Weight of portion dissolved by alcohol, 3.4
Weight of residue, 6.9

Taking the averages of the figures representing the ethoxy and hydrogen products, we find that they stand in the relation of 4.05 to 7.28, indicating that the ethoxy product forms 35.8 per cent. of the total. It will be noticed that this figure is nearly 8 per cent. lower than that obtained when absolute alcohol was used in the decomposition.

Experiments with 90-per cent. Alcohol.—I. 9.8 grams of diazo compound were decomposed in 200 cc. of 90-per cent. alcohol. The odor of aldehyde was strong. The decomposition was more rapid than before, being complete in about fifteen minutes. The color of the solution was deeper than in any previous case. The barium salts dried, as well as the extracted ethoxy portion, showed more color than before.

Weight of barium salts,	12.38 grams.
[A] Weight of portion dissolved by alcohol,	5.40
[B] Weight of residue,	6.65

Analysis of [A].—0.2812 gram of anhydrous salt gave 0.1181 gram of barium sulphate.

$$\text{Calculated for } C_6H_3{-}\overset{\diagup CH_3}{\underset{\diagdown O.C_2H_5}{SO_3ba.}}$$

	Calculated	Found.
Ba	24.16	24.66

Analysis of [B].—0.2444 gram of anhydrous salt gave 0.1223 gram of barium sulphate.

$$\text{Calculated for } C_6H_4{<}\overset{CH_3}{\underset{SO_3ba.}{}}$$

	Calculated	Found.
Ba	28.60	28.26

II. 9 grams of diazo compound were decomposed in 200 cc. of 90-per cent. alcohol. The same phenomena were noted as in the preceding case.

Weight of barium salts,	10.98 grams.
Weight of portion dissolved by alcohol,	4.93
Weight of residue,	6.03

III. 9.75 grams of diazo compound were decomposed in 200 cc. of 90-per cent. alcohol.

Weight of barium salts,	12.00 grams.
Weight of portion dissolved by alcohol,	5.58
Weight of residue,	6.24

The averages, taken as before, for this series of experiments stand in the relation of 5.3 to 6.3, the ethoxy product constituting 45.7 per cent. of the total. From the relation of the results of the two preceding series a lower figure was expected. A smaller proportion of the ethoxy body was obtained in the experiments with 95-per cent. alcohol than when absolute alcohol was used. The marked presence of color in the products from this series of experiments is suggestive of other reactions than those under discussion. It is possible that the small amount of water present gave rise to phenol reactions. It may have been due to this fact that the separation of the products as indicated by the analyses was not so sharp as in preceding cases. The tendency here mentioned showed itself in greater degree when still more dilute alcohol was used in the decomposition.

Experiments with 85-per cent. Alcohol.—I. 9.9 grams of diazo compound were decomposed in 200 cc. of 85-per cent. alcohol. A strong odor of aldehyde was perceptible. The decomposition was complete in about twelve minutes. The color of the solution during the reaction was a muddy brown, changing to deep garnet-red as it neared completion. The dried barium salts showed yellow color. The extracted ethoxy salt was brownish red when dried.

Weight of barium salts, 12.02 grams.
[A] Weight of portion dissolved by alcohol, 6.14
[B] Weight of residue, 5.85

Analysis of [A].—0.2381 gram of anhydrous salt gave 0.1011 gram of barium sulphate.

$$\text{Calculated for } C_6H_3 \underset{\overset{\displaystyle -SO_3ba.}{\diagdown O.C_2H_5}}{\overset{\diagup CH_3}{}}$$

	Calculated	Found.
Ba	24.16	25.04

Analysis of [B].—0.2545 gram of anhydrous salt gave 0.1229 gram of barium sulphate.

$$\text{Calculated for } C_6H_4 \underset{SO_3ba}{\overset{CH_3}{<}}.$$

	Calculated	Found.
Ba	28.60	28.57

The results show the portion [B] to have been very pure. Granting that the ethoxy salt was contaminated by the presence of some hydrogen salt only, the figures that would more nearly represent the relative quantities of the two products would be:

Weight of ethoxy salt, 5.23 grams.
Weight of hydrogen salt, 6.76

It is doubtful, from what was said under the preceding experiment, whether it is right to assume that the impurity consisted entirely of the hydrogen salt.

II. 10.2 grams of diazo compound were decomposed in 200 cc. of 85-per cent. alcohol. The decomposition was complete in ten minutes. The same color was noted in the products as in the preceding experiment.

Weight of barium salts,	12.43 grams.
[A] Weight of portion dissolved by alcohol,	4.57
[B] Weight of residue,	7.63

Analysis of [A].—0.2232 gram of anhydrous salt gave 0.0954 gram of barium sulphate.

$$\text{Calculated for } C_6H_3-SO_3ba \cdot \overset{/CH_3}{\underset{\backslash O.C_2H_5}{}}$$

	Calculated	Found.
Ba	24.16	25.08

Analysis of [B].—0.2435 gram of anhydrous salt gave 0.1143 gram of barium sulphate.

$$\text{Calculated for } C_6H_4 < \overset{CH_3}{\underset{SO_3ba}{}}$$

	Calculated	Found.
Ba	28.60	27.55

In this experiment it will be seen that the two products were not separated by boiling with alcohol in the usual way. In the cases in which strong alcohol was used in the decomposition, the dissolving action of the alcohol used in extraction was found to be sharp. If just the right quantity was used the separation was satisfactory. If too much was used, all the ethoxy product was dissolved together with some of the other, the analyses showing a high percentage of barium for the former, but nearly theoretical for the residue. If the quantity of alcohol was insufficient for the extraction of the ethoxy salt, the residual product showed a low percentage of barium, the ethoxy portion appearing pure. In either case one of the products seemed to be fairly pure. In the analyses just given it will be seen that neither product appears to have been pure, and it is probable that foreign matter was present, due to the dilution of the alcohol used in the decomposition.

III. 10 grams of diazo compound were decomposed in 200 cc. of 85-per cent. alcohol. The same facts were noted as in the last two decompositions.

Weight of barium salts, 12.44 grams.
Weight of portion dissolved by alcohol, 5.20
Weight of residue, 7.23

Although, for the reasons given, not too great reliance should be placed upon the results of the experiments of this series, it may be well to take the averages of the figures as obtained. They stand in the ratio of 4.99 to 7.20, the ethoxy compound representing 40.9 per cent. of the total. This figure lies between those found for cases in which absolute and 95-per cent. alcohols were used.

Experiments with 80-*per cent. Alcohol.*—The decompositions in 80-per cent. alcohol are of interest only in so far as they show to a greater degree the tendencies noticed in the last series. The decomposition was very rapid. The products were deeply colored. The separation by means of alcohol was entirely unsatisfactory. The extracted portions, on evaporation to dryness, showed a deep scarlet color. The relative quantities of the separated products differed so widely that no definite conclusions can be drawn from the three experiments made.

No further experiments were made on the influence of dilution of the alcohol on the reactions.

A brief summary of results follows :

Pressure constant. Strength of Alcohol used in decomposition.	Ethoxy Product.
Absolute	43.4 per cent.
Ninety-five per cent.	35.8
Ninety per cent.	47.7
Eighty-five per cent.	40.9
Eighty per cent.	...

The main conclusions from these experiments are as follows:

I. The presence of small quantities of water in the alcohol has little influence on the course of the reactions in the decomposition of the diazo compound.

II. The presence of more than 15 per cent. of water gives rise to other reactions than those involved in the decomposition of the diazo body to toluenesulphonic acid and to ethoxytoluenesulphonic acid. The formation of phenol bodies probably takes place. The fact that the decomposition in dilute alcohol is much more rapid than in strong alcohol is suggestive.

II.—Decomposition of the Diazo Compound in Absolute Alcohol, the Pressure being Varied.

The lowest pressure at which Remsen and Palmer were able to obtain satisfactory results was 120 mm. The highest that could be measured by the manometer used in these experiments was 800 mm. Accordingly, eight series of decompositions were made at intervals of pressure between these limits. The experiments were conducted in the manner already described. The separation of the two products was effected by extraction with 250 cc. of 94-per cent. alcohol, except in cases of very high pressures, when this quantity was found insufficient.

Experiments at 120 *mm. Pressure.*—I. 9.5 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The odor of aldehyde was very strong. The action continued about forty minutes. There was considerable color in the solution during and after decomposition. But little color was noticeable in the dried barium salts.

Weight of barium salts,	11.62 grams.
[A] Weight of portion dissolved by alcohol,	4.3
[B] Weight of residue,	7.20

Analysis of [A].—0.2442 gram of anhydrous salt gave 0.1033 gram of barium sulphate.

$$\text{Calculated for } C_6H_3 \overset{\diagup CH_3}{\underset{\diagdown O.C_2H_5}{-SO_3ba.}}$$

		Found.
Ba	24.16	24.84

Analysis of [B].—0.2416 gram of anhydrous salt gave 0.1166 gram of barium sulphate.

$$\text{Calculated for } C_6H_4 {\diagdown \atop <} {CH_3 \atop SO_3ba.}$$

		Found.
Ba	28.60	28.33

It would appear that the number representing the ethoxy product was too great.

II. 10.2 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as before.

Weight of barium salts,	12.22 grams.
Weight of portion dissolved by alcohol,	4.07
Weight of residue,	8.12

These figures correspond very nearly to those that would be obtained from the preceding experiment if correction were made according to the results of the analyses.

III. 9.3 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	11.26 grams.
Weight of portion dissolved by alcohol,	4.60
Weight of residue,	6.55

Although the results of this experiment differ considerably from those of the two preceding it, still in all three the hydrogen reaction is evidently the principal one. The averages stand in the ratio of 4.32 to 7.29, the ethoxy compound representing 37.2 per cent. of the total.

Experiments at 210 *mm. Pressure.*—I. 8 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

The points noted were practically the same as in the preceding series. The color of the solution was cherry red. The barium salts showed no color.

Weight of barium salts,	9.03 grams.
[A] Weight of portion dissolved by alcohol,	3.42
[B] Weight of residue,	5.44

Analysis of [A].—0.2386 gram of anhydrous salt gave 0.1005 gram of barium sulphate.

$$\text{Calculated for } C_6H_3{-}SO_3ba\diagdown{}^{CH_3}_{O.C_2H_5}$$

	Calculated	Found.
Ba	24.16	24.72

Analysis of [B].—0.2493 gram of anhydrous salt gave 0.1209 gram of barium sulphate.

$$\text{Calculated for } C_6H_4\diagdown{}^{CH_3}_{SO_3ba}.$$

	Calculated	Found.
Ba	28.60	28.47

II. 9.5 grams of the diazo body were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	11.73 grams.
Weight of portion dissolved by alcohol,	4.54
Weight of residue,	7.11

The proportion of ethoxy product appeared so small that it seemed probable that all had not been extracted. The hydrogen portion was accordingly boiled with alcohol once more. Only about 0.3 gram was dissolved out.

III. 9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	10.83 grams.
Weight of portion dissolved by alcohol,	4.70
Weight of residue,	5.97

The averages taken as before stand in the ratio 4.22 to 6.17, indicating that the ethoxy compound made 40.6 per cent. of the total.

Experiments at 300 mm. Pressure.—The decompositions in absolute alcohol at 300 mm. pressure have been discussed. They indicated that the ethoxy product constitutes 43.4 per cent. of the total.

Experiments at 400 mm. Pressure.—I. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. A strong odor of aldehyde was noticed. The decomposition was complete in a little less than half an hour. The other points noted were about as in the series at 300 mm. pressure.

Weight of barium salts,	11.74 grams.
[A] Weight of portion dissolved by alcohol,	5.75
[B] Weight of residue,	5.85

Analysis of [A].—0.2368 gram of anhydrous salt gave 0.0991 gram of barium sulphate.

$$\text{Calculated for } C_6H_3{-}SO_3ba{\Big\langle}{\overset{CH_3}{\underset{O.C_2H_5}{}}}$$

		Found.
Ba	24.16	24.56

Analysis of [B].—0.2216 gram of anhydrous salt gave 0.1070 gram of barium sulphate.

$$\text{Calculated for } C_6H_4{<}{\overset{CH_3}{\underset{SO_3ba}{}}}.$$

		Found.
Ba	28.60	28.34

II. 8.9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	10.89 grams.
Weight of portion dissolved by alcohol,	5.37
Weight of residue,	5.41

III. 9.9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	12.37 grams.
Weight of portion dissolved by alcohol,	5.72
Weight of residue,	6.41

The averages stand to each other as 5.61 to 5.89, the ethoxy compound constituting 48.7 per cent. of the total.

Experiments at 500 *mm. Pressure.*—I. 8.4 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The odor of aldehyde was not so strong as in previous experiments. The decomposition lasted about twenty minutes. There was less color in the solution during and after decomposition than before, and the dried barium salts were practically white.

> Weight of barium salts, 10.58 grams.
> [A] Weight of portion dissolved by alcohol, 4.40
> [B] Weight of residue, 6.02

It was noticed, on extraction with alcohol, that the filtered portion, on cooling very slightly, deposited an unusually large quantity of crystalline ethoxy salt. This evident saturation of the solution raised doubt as to the completeness of the extraction of the ethoxy salt. The analyses of the products confirmed the doubt.

Analysis of [A].—0.2507 gram of anhydrous salt gave 0.1049 gram of barium sulphate.

$$\text{Calculated for } C_6H_3-SO_3\text{ba.}\begin{smallmatrix}\diagup CH_3 \\ \diagdown O.C_2H_5\end{smallmatrix}$$

	Calculated	Found.
Ba	24.16	24.55

Analysis of [B].—0.2782 gram of anhydrous salt gave 0.1328 gram of barium sulphate.

$$\text{Calculated for } C_6H_4 < \begin{smallmatrix} CH_3 \\ SO_3\text{ba} \end{smallmatrix} .$$

	Calculated	Found.
Ba	28.60	28.01

Calculating from the analyses, the numbers that would more nearly represent the two weights would be :

> Weight of ethoxy salt, 5.30 grams.
> Weight of hydrogen salt, 5.12

II. 8.8 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The experiment was conducted in the same way as the preceding one, and with like results.

> Weight of barium salts, 12.85 grams.
> Weight of portion dissolved by alcohol, 5.92
> Weight of residue, 6.8

The corrected numbers are :

> Weight of ethoxy salt, 6.89 grams.
> Weight of hydrogen salt, 5.83

III. 10.4 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	12.87 grams.
[A] Weight of portion dissolved by alcohol,	5.90
[B] Weight of residue,	6.82

Analysis of [A].—0.2772 gram of anhydrous salt gave 0.1152 gram of barium sulphate.

$$\text{Calculated for } C_6H_3-SO_3ba\begin{smallmatrix}\diagup CH_3\\\diagdown O.C_2H_5\end{smallmatrix}.$$

	Calculated for $C_6H_3-SO_3ba\begin{smallmatrix}\diagup CH_3\\\diagdown O.C_2H_5\end{smallmatrix}$	Found.
Ba	24.16	24.43

Analysis of [B].—0.2665 gram of anhydrous salt gave 0.1275 gram of barium sulphate.

	Calculated for $C_6H_4\begin{smallmatrix}\diagup CH_3\\\diagdown SO_3ba\end{smallmatrix}$.	Found.
Ba	28.60	28.09

The corrected numbers would be:

Weight of ethoxy salt,   6.75 grams.
Weight of hydrogen salt, 5.97

The averages for this series stand in the ratio of 6.31 to 5.64, the ethoxy compound constituting 52.8 per cent. of the total.

This is the first series of experiments in which the ethoxy product was formed in greater quantity than the other. According to the results, the ethoxy reaction predominates over the other but very little. Remsen and Palmer were led to the conclusion that at this pressure it is the sole reaction.

Experiments at 600 *mm. Pressure.*—I. 9.3 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. There was little odor of aldehyde perceptible. The decomposition was complete in about twelve minutes. There was less color in the products of decomposition than in any previous experiment.

Weight of barium salts,	11.84 grams.
Weight of portion dissolved by alcohol,	6.8
Weight of residue,	4.9

II. 8.8 grams of the diazo body were decomposed in 200 cc. of absolute alcohol. The same points were noted as in the preceding experiment.

Weight of barium salts,	11.22 grams.
Weight of portion dissolved by alcohol,	6.02
Weight of residue,	5.08

III. 10 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts, 12.21 grams.
[A] Weight of portion dissolved by alcohol, 7.3
[B] Weight of residue, 4.8

Analysis of [A].—0.2493 gram of anhydrous salt gave 0.1035 gram of barium sulphate.

$$\text{Calculated for } C_6H_3{\diagup}^{CH_3}_{\diagdown O.C_2H_5}{-}SO_3ba.$$

	Calculated for $C_6H_3{-}SO_3ba$, $O.C_2H_5$	Found.
Ba	24.16	24.37

Analysis of [B].—0.2327 gram of anhydrous salt gave 0.1117 gram of barium sulphate.

	Calculated for $C_6H_4{<}^{CH_3}_{SO_3ba}$.	Found.
Ba	28.60	28.16

It was found necessary in this series to increase the quantity of alcohol used in the separation to 300 cc. The averages of the weights of the two products obtained stand in the ratio of 6.7 to 4.9, the ethoxy compound constituting 57.7 per cent. of the total— a marked increase over the result of the last series of experiments.

Experiments at 700 mm. Pressure.—Four decompositions were made at this pressure.

I. 10.7 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. A very faint odor of aldehyde was perceptible at the valve. The decomposition was complete in eight minutes. The solution after decomposition showed a light yellow color; the dried barium salts, none at all. It was necessary to use 350 cc. of alcohol in extracting the ethoxy salt.

Weight of barium salts, 10.73 grams.
[A] Weight of portion dissolved by alcohol, 6.74
[B] Weight of residue, 3.92

Analysis of [A].—0.2312 gram of anhydrous salt gave 0.0974 gram of barium sulphate.

	Calculated for $C_6H_3{-}SO_3ba$. $O.C_2H_5$	Found.
Ba	24.16	24.72

Analysis of [B] was thought to be unnecessary.

II. 9.4 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as in the preceding experiment.

Weight of barium salts, 11.34 grams.
Weight of portion dissolved by alcohol, 7.11
Weight of residue, 4.15

III. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts, 12.36 grams.
Weight of portion dissolved by alcohol, 7.91
Weight of residue, 4.34

IV. 9.3 grams of diazo compound were dissolved in 200 cc. of absolute alcohol.

Weight of barium salts, 11.24 grams.
Weight of portion dissolved by alcohol, 6.88
Weight of residue, 4.26

The averages of the numbers representing the two products stand in the ratio of 7.16 to 4.17, the ethoxy compound constituting 62.2 per cent. of the total. There is greater difference between this number and that obtained in the last series, than between the latter and that preceding it. This fact is suggestive. The same tendency will be noticed in the next series.

Experiments at 800 *mm. Pressure.*—I. 10 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. There was little, if any, odor of aldehyde perceptible. The decomposition was more rapid than in any previous experiment with strong alcohol, being complete in five minutes. The solution after decomposition was colored a pale yellow. Indeed it appears that the higher the pressure at which the decomposition is made, the cleaner is the reaction. The barium salts were entirely free from color.

Weight of barium salts, 12.07 grams.
[A] Weight of portion dissolved by alcohol, 8.60
[B] Weight of residue, 3.30

Analysis of [A].—0.2319 gram of anhydrous salt gave 0.0963 gram of barium sulphate.

$$\text{Calculated for } C_6H_3 {\overset{\text{CH}_3}{\underset{\text{O.C}_2H_5}{-SO_3\text{ba}\cdot}}}$$

	Calculated	Found.
Ba	24.16	24.37

Analysis of [B].—0.2102 gram of anhydrous salt gave 0.1017 gram of barium sulphate.

	Calculated for $C_6H_3<^{CH_3}_{SO_3ba}$.	Found.
Ba	28.60	28.40

II. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as before.

Weight of barium salts,	12.01 grams.
Weight of portion dissolved by alcohol,	8.19
Weight of residue,	3.79

III. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	11.7 grams.
Weight of portion dissolved by alcohol,	8.02
Weight of residue,	3.57

The averages, taken as in former cases, stand in the ratio of 8.24 to 3.55, the ethoxy compound representing 69.8 per cent. of the total.

The experiments at 800 mm. pressure conclude the decompositions made by us. It will be noticed that in each series there are small differences in the relative quantities of the two products obtained. These discrepancies may be due to actual lack of constancy in the course of the reactions, but are more probably owing to imperfections in the method of work. There is evidently a marked tendency in the results that is unmistakable. It was suggested by Remsen and Palmer that increased pressure favors the ethoxy reaction. The results here recorded confirm this conclusion. Summarising these results at the various pressures, we find a remarkable degree of regularity in the increase of the proportion of ethoxy product with increase of pressure.

Pressure.	Ethoxy Product.
120 mm.	37.2 per cent.
210	40.6
300	43.4
400	48.7
500	52.8
600	57.7
700	63.2
800	69.8

With one exception, the differences between the percentages of ethoxy product for proximate experiments increase slightly as the pressure is increased. A curve representing the course of the reaction as influenced by pressure is given on the accompanying page. It approximates very nearly to a parabola, the point lying farthest from the curve being out of position only one per cent.

III.—Influence of Temperature in the Decomposition of the Diazo Compound.

A question will naturally suggest itself as regards the temperature at which the decompositions were effected. Boiling under increased pressure requires, of course, a higher temperature than boiling at lower pressure. It was noticed that the decomposition usually began immediately upon boiling, but constant boiling was not necessary for its continuance. Experiments were made with a view to ascertaining the temperature of the alcohol during decomposition under the various conditions of pressure. The following results were obtained in several series of observations:

Pressure.	Temperature.
120 mm.	$84°$
210	87
300	90
400	$92\frac{1}{2}$
500	$94\frac{1}{2}$
600	97
700	99
800	102

The network of wire and the curvature of the sides of the flask rendered close reading impossible. As far as could be observed, the temperature during decomposition at any given pressure remained constant.

The question whether the difference in the course of the reactions involved in the decomposition at different pressures is due directly to change in pressure or to change of temperature caused by change of pressure, cannot be answered definitely by the aid of the experiments described above. In all of them the desired pressure was obtained by heating the flask rapidly, until the alcohol vapors and nitrogen given off in decomposition produced

ETHOXY PRODUCT MEASURED IN PER CENT OF TOTAL
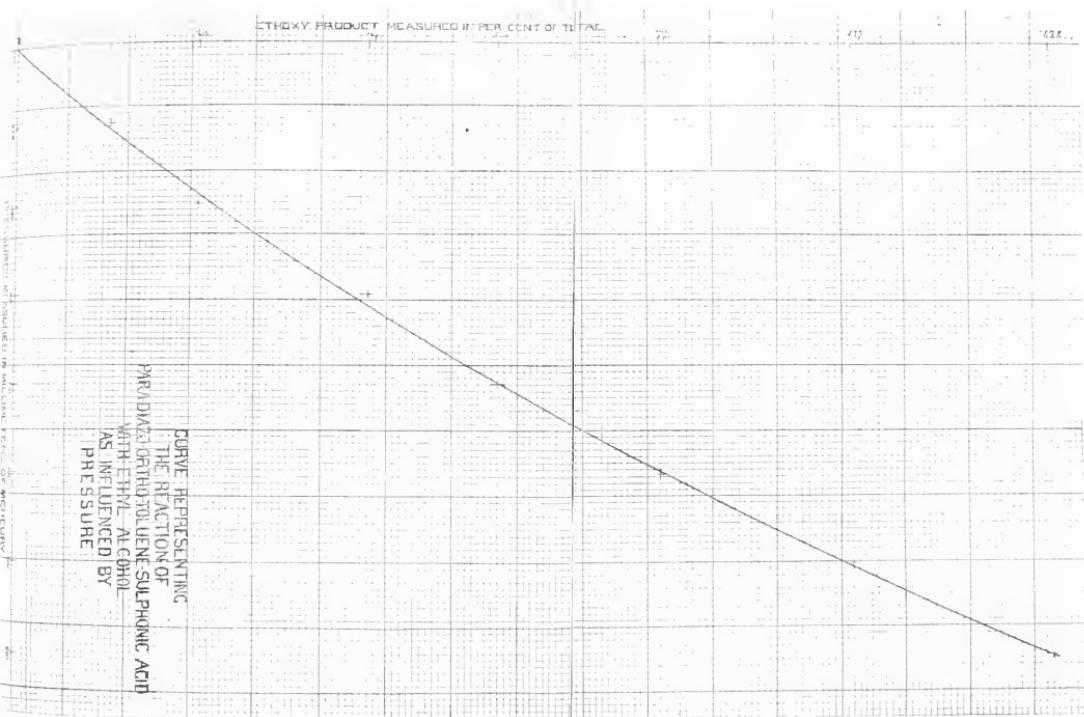
CURVE REPRESENTING
THE REACTION OF
PARADIAZO ORTHO-TOLUENE-SULPHONIC ACID
WITH ETHYL ALCOHOL
AS INFLUENCED BY
PRESSURE

the desired effect. To decide the question at issue, the following experiments were tried : The decomposition flask was connected through suitable drying apparatus with a second balloon flask containing a strong solution of ammonium nitrite. By warming this nearly to the boiling-point, nitrogen was given off freely. The pressure was regulated by the valve connected with the flask, and was measured in the usual way by the manometer in connection with the decomposition flask. It was thus found possible to produce any desired pressure without introducing any substance not already present in the products of decomposition, and maintain it very constantly quite independently of the temperature of the contents of the decomposition flask. The desired pressure being established, the flask was heated to any desired temperature. It was found that at low temperature and high pressure the diazo compound was not decomposed. On raising the temperature gradually, decomposition began when it approached the boiling-point of alcohol under the pressure maintained in the experiment. On the other hand, keeping the lower temperature, and lowering the pressure, little decomposition was noticed until like conditions as to temperature and pressure were produced. In other words, it appears that for decomposition at any given pressure, a definite temperature is necessary, and this temperature lies very near the point at which the alcohol boils at that pressure. The temperature being kept constant, if the pressure be increased, decomposition is interfered with. The reason for this is unknown.

The decomposition of the diazo compound appears to be influenced by temperature as well as by pressure. To which should be ascribed the cause of the regular differences noted in the experiments under the various conditions, it is impossible at present to say.

PARAETHOXYORTHOTOLUENESULPHONIC ACID AND SOME OF ITS DERIVATIVES.

By Paul J. Dashiell.

In the course of the investigation the results of which are described in the preceding article, a considerable quantity of the barium salt of paraethoxyorthotoluenesulphonic acid was collected, and as but few of its derivatives had been previously made, I prepared and studied some of these. The amide made in the usual way was found to melt at $143°–144°$, as stated by Remsen and Palmer.[1]

Paraethoxyorthotoluenesulphonic Acid, $C_6H_3-SO_3H(o).\begin{smallmatrix}\diagup CH_3\\ \diagdown O.C_2H_5(p)\end{smallmatrix}$

Made from the purified barium salt (description given below) by precipitating the metal exactly with dilute sulphuric acid—forms a brownish yellow, crystalline, hygroscopic mass, difficult to dry. No analysis was made. The acid was used in the preparation of various salts.
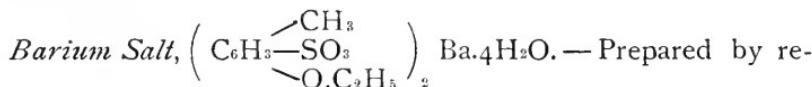
Barium Salt, $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -SO_3\\ \diagdown O.C_2H_5\end{smallmatrix}\right)_2 Ba.4H_2O.$ — Prepared by repeated recrystallisation from alcohol and water of the crude product obtained from the decompositions; forms white, shining leaflets, apparently of the monoclinic system; fairly soluble in cold water, readily in hot water; difficultly soluble in cold alcohol, more readily in hot alcohol.

0.2531 gram of salt lost at $150°$ C. 0.0282 gram of water and gave 0.0922 gram of barium sulphate.

0.2539 gram of salt lost 0.0287 gram of water and gave 0.0920 gram of barium sulphate.
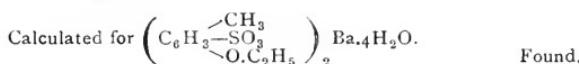
	Calculated for $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -SO_3\\ \diagdown O.C_2H_5\end{smallmatrix}\right)_2 Ba.4H_2O.$	Found.
H_2O	11.26	11.14–11.30
Ba	21.44	21.42–21.38

Lead Salt, $\left(C_6H_3\begin{smallmatrix}\diagup CH_3\\ -SO_3\\ \diagdown O.C_2H_5\end{smallmatrix}\right)_2 Pb.3H_2O.$ — Prepared by neutralisation of the acid with excess of pure lead carbonate; forms

[1] This Journal **8**, 243.

colorless, well-formed, lustrous leaflets, arranged in radial clusters; sparingly soluble in cold water and in alcohol, very soluble in both when hot.

0.2223 gram of salt lost at 130° C. 0.0177 gram of water and gave 0.0969 gram of lead sulphate.

0.1995 gram of salt lost 0.0158 gram of water and gave 0.0863 gram of lead sulphate.

Calculated for $\left(C_6H_3{-}SO_3{<}^{CH_3}_{O.C_2H_5} \right)_2 Pb.3H_2O.$

		Found.
H_2O	7.82	7.96– 7.91
Pb	29.85	29.72–29.50

Calcium Salt, $\left(C_6H_3{-}SO_3{<}^{CH_3}_{O.C_2H_5} \right)_2 Ca.3H_2O.$—Prepared by neutralisation of the free acid with finely divided calcite; forms lustrous, prismatic crystals, showing tendency to penetration twinning; exceedingly soluble in water, fairly soluble in alcohol.

0.2524 gram of salt lost at 230° C. 0.0266 gram of water and gave 0.0660 gram of calcium sulphate.

0.2421 gram of salt lost 0.0250 gram of water and gave 0.0633 gram of calcium sulphate.

Calculated for $\left(C_6H_3{-}SO_3{<}^{CH_3}_{O.C_2H_5} \right)_2 Ca.3H_2O.$

		Found.
H_2O	10.30	10.53–10.32
Ca	7.63	7.64– 7.43

Magnesium Salt, $\left(C_6H_3{-}SO_3{<}^{CH_3}_{O.C_2H_5} \right)_2 Mg.5H_2O.$—Prepared by neutralisation of the acid with pure magnesium carbonate; crystallises in long, narrow plates, more than an inch long, closely matted together and showing transverse striations, apparently due to twinning; fairly soluble in water, less so in alcohol.

0.2037 gram of salt lost at 135° C. 0.0338 gram of water and gave 0.0465 gram of magnesium sulphate.

0.2243 gram of salt lost 0.0374 gram of water and gave 0.0478 gram of magnesium sulphate.

Calculated for $\left(C_6H_3{-}SO_3{<}^{CH_3}_{O.C_2H_5} \right)_2 Mg.5H_2O.$

		Found.
H_2O	16.53	16.59–16.32
Mg	4.48	4.56– 4.30

Zinc Salt, $\left(C_6H_3 \diagdown{}^{CH_3}_{S_2O} \diagup{}_{O.C_2H_5} \right)_2 Zn.6H_2O.$—Prepared by neutralisation of the acid with pure zinc carbonate; crystallises remarkably well in thick, colorless, transparent, striated plates; easily soluble in water and alcohol.
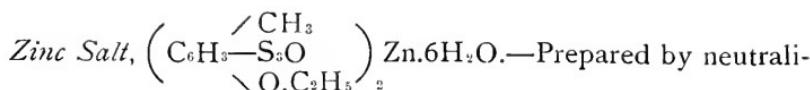
0.2291 gram of salt lost at 150° C. 0.0406 gram of water and gave 0.0606 gram of zinc sulphate.

0.2511 gram of salt lost 0.0454 gram of water and gave 0.0666 gram of zinc sulphate.

	Calculated for $\left(C_6H_3 \diagdown{}^{CH_3}_{SO_3} \diagup{}_{O.C_2H_5} \right)_2 Zn.6H_2O.$	Found.
H_2O	17.91	17.81–17.84
Zn	10.85	10.71–10.70

Copper Salt, $\left(C_6H_3 \diagdown{}^{CH_3}_{SO_3} \diagup{}_{O.C_2H_5} \right)_2 Cu.6H_2O.$—Prepared by saturation of the free acid with pure copper oxide; forms thick, lustrous, pale-green plates, closely massed together and showing transverse striations due to twinning; readily soluble in alcohol and water.
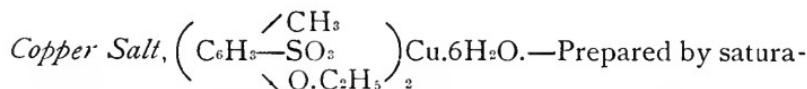
0.2441 gram of salt lost at 150° C. 0.0444 gram of water.

0.2350 gram of salt lost 0.0426 gram of water and gave 0.0307 gram of copper oxide.

0.2311 gram of salt gave 0.0301 gram of copper oxide.

	Calculated for $\left(C_6H_3 \diagdown{}^{CH_3}_{SO_3} \diagup{}_{O\,C_2H_5} \right)_2 Cu.6H_2O.$	Found.
H_2O	17.97	18.18–18.12
Cu	10.52	10.40–10.38

Silver Salt.—Prepared by neutralisation of the acid with pure silver carbonate; crystallises beautifully in well-formed prisms; easily affected by the light, with deposition of silver oxide. Analyses were unsatisfactory on this account.

Potassium Salt, $C_6H_3 \diagdown{}^{CH_3}_{SO_3K.H_2O.}$—Prepared by exact precipitation of the metal from the barium salt by a solution of potassium carbonate; very soluble in water, but obtained, after evaporation to a small volume, in white leaflets; difficultly soluble in cold alcohol.

0.2622 gram of salt lost at 180° C. 0.0185 gram of water and gave 0.0872 gram of potassium sulphate.

0.2778 gram of salt lost 0.0190 gram of water and gave 0.0916 gram of potassium sulphate.

Calculated for $C_6H_3\genfrac{}{}{0pt}{}{CH_3}{}{-SO_3K.H_2O.}\genfrac{}{}{0pt}{}{}{O.C_2H_5}$

	Calculated	Found.
H₂O	6.62	6.63– 6.76
K	14.88	14.89–14.77

Sodium Salt.—Prepared by neutralisation of the free acid with pure sodium carbonate; so readily soluble in water that evaporation to dryness was necessary in order to obtain it; less soluble in alcohol.

0.2560 gram of anhydrous salt gave 0.0779 gram of sodium sulphate.

0.2453 gram of anhydrous salt gave 0.0753 gram of sodium sulphate.

Calculated for $C_6H_3\genfrac{}{}{0pt}{}{CH_3}{}{-SO_3Na.}\genfrac{}{}{0pt}{}{}{O.C_2H_5}$

	Calculated	Found.
Na	9.64	9.85–9.94

A little of the carbonate was probably present.

Ammonium Salt.—Prepared by neutralisation of the acid with ammonia, driving off the excess on the water-bath and evaporating to dryness, when the salt was obtained as a crystalline yellowish crust, whose underside showed small, shining, platelike, colorless crystals. No analyses were made.

Chloride of paraethoxyorthotoluenesulphonic Acid,

$C_6H_3\genfrac{}{}{0pt}{}{CH_3}{}{-SO_2Cl(o).}\genfrac{}{}{0pt}{}{}{O.C_2H_5(p)}$—Prepared by treatment of the dried and powdered sodium salt with a small excess of phosphorus pentachloride as described in connection with the amide—appeared as a clear, light-brown, mobile oil, with odor characteristic of acid chlorides. Treatment with benzene and with ether failed to produce change beyond mechanical solution, from which the oil was again obtained on distillation of the solvent.

LXXV.—ON CERTAIN DERIVATIVES OF PYRO-MUCAMIDE.[1]

By Charles E. Saunders.

This investigation was undertaken at the suggestion of Professor H. B. Hill, in the hope of obtaining from pyromucamide or its derivatives, through Hoffmann's[2] reaction, an amine having the nitrogen atom directly united to a carbon atom of the furfuran ring, no such amine being at present known. Since preliminary experiments with pyromucamide had shown that the reaction was complicated by products formed through the action of the bromine upon the furfuran group, $\beta\delta$-dibrompyromucamide was chosen as better adapted to the purpose, since the corresponding acid is unaffected by bromine. In this case, however, the product proved to be the nitrile of the acid, instead of the amine with one less carbon atom. The behavior of pyromucamide with dry bromine was next studied, and a stable tetrabromide isolated, and at the same time the action of bromine in aqueous solution upon pyromucamide was examined in order to find an explanation of certain striking color reactions which had previously been observed in this laboratory.

The Action of Bromine and Potassium Hydroxide on $\beta\delta$-Dibrompyromucamide.

Bromine alone has no marked action on $\beta\delta$-dibrompyromucamide, the amide dissolving quietly in the bromine. On evaporating, the amide can be recovered unchanged, though the removal of the last portions of bromine at ordinary temperatures occupies considerable time, indicating perhaps the production of an unstable tetrabromide. Nevertheless, all attempts to prove more definitely the formation of such a product failed. When the amide was dissolved in bromine and the solution treated with aqueous potassium hydroxide, a small yield of a substance insoluble in water was obtained. This was filtered off, washed with water, and

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[1] Presented by Henry B. Hill at a meeting of the American Academy of Arts and Sciences, held November 9, 1892.

[2] Ber. d. chem. Ges. **14,** 2725; **15,** 407, 752, 762; **17,** 1406, 1923; **18,** 2734.

distilled with steam. The best yield was obtained as follows. One part of the amide was dissolved in 1.8 parts of bromine (about six atoms of bromine to one molecule of amide) in a large beaker. Over this solution was poured a considerable quantity of a cold five per cent. solution of sodium or potassium hydroxide. The contents of the beaker were kept cold, and allowed to stand, the alkaline reaction being maintained by the occasional addition of a small portion of 20 per cent. sodium hydroxide solution. The insoluble product gradually rose to the surface, as the bromine disappeared, and was skimmed off. It was washed with dilute acid, and then distilled with steam. The yield was nearly 13 per cent. of the weight of amide taken. For further purification the substance was crystallised from a very small quantity of alcohol, solution being brought about at 90° to 100° under pressure.

The substance gave the following results on analysis:

I. 0.4259 gram substance gave 0.3745 gram CO_2 and 0.0160 gram H_2O.

II. 0.2044 gram substance gave 0.3082 gram AgBr.

III. 0.2056 gram substance gave 10.3 cc. of moist nitrogen at 15.3° and 757.5 mm. pressure.

	Calculated for C_5HBr_2NO.	I.	Found. II.	III.
C	23.90	23.98	...	...
H	0.40	0.42	...	...
Br	63.75	...	64.17	...
N	5.58	...	...	5.84

The analysis shows that the substance is not the expected amine, but is $\beta\delta$-dibromfurfuronitrile. This conclusion was confirmed by the reactions of the substance, and by its preparation through the dehydration of the amide, using phosphorus pentachloride as the dehydrating agent. The amide was mixed with the calculated quantity of phosphorus pentachloride, and the mixture heated in a distilling flask to about 200°, until hydrochloric acid ceased to be given off. The contents of the flask were then distilled with steam. The yield of dibromfurfuronitrile was 56 per cent. of the calculated amount. The substance as thus obtained was found to be identical in composition and physical properties with that formed by the action of bromine and dilute potassium hydroxide on the dibromamide. A combustion of this product gave the following results:

0.4272 gram substance gave 0.3793 gram CO_2 and 0.0217 gram H_2O.

	Calculated for C_5HBr_2NO.	Found.
C	23.90	24.21
H	0.40	0.56

Properties of βδ-Dibromfurfuronitrile.—It is a colorless solid, possessing a characteristic and rather pleasant odor. It is volatile with steam, scarcely at all soluble in water, readily soluble in ether and in hot alcohol (especially at 100° under pressure). Its melting-point is 88° (uncor.), and its boiling-point 225° (uncor.). It can be sublimed. It crystallises from superheated alcohol in leaflets or plates. On standing for several days in a warm room with concentrated hydrochloric acid, it is converted into βδ-dibrom-pyromucamide. When it is heated for about an hour in a sealed tube at 100° with concentrated hydrochloric acid, a considerable amount of βδ-dibrompyromucic acid is formed. Prolonged heating causes blackening.

These two reactions were tried with the nitrile prepared in both ways. In alcoholic solution sodium amalgam formed no reduction product. The nitrile was dissolved in dilute alcohol, and treated with two per cent. sodium amalgam, a current of carbon dioxide being passed through until the action was over. The distillate obtained from this was not alkaline, and gave practically no residue when acidified and evaporated. The residue in the flask gave, on evaporation, needles of βδ-dibrompyromucamide.

When the solution of dibromamide in bromine was treated with dilute cold potassium or sodium hydroxide, the only product found, beside the nitrile, was monobrommaleic acid. This was identified by its melting-point and other physical properties, as well as those of its barium salt.

The dehydration of the dibromamide—under the conditions of the experiments related—with formation of the nitrile, is particularly interesting, because Hofmann[1] found that, in preparing amines from amides by the method introduced by him, nitriles were sometimes produced, chiefly when working with the amides of the higher fatty acids; but the nitriles thus formed always contained one carbon atom less than the amide with which he started, and he considers the amine to be an intermediate product in these cases. In the present instance, however, since the nitrile contains the

[1] Ber. d. chem. Ges. **17**, 1406, 1920.

same number of carbon atoms as the amide, this interpretation of the reaction cannot be applied. The author has no explanation to offer. It is worthy of note that the same reaction takes place, whether the alkali used is potassium, sodium, or barium hydroxide.

The Action of Bromine on Pyromucamide.

The tetrabromide of pyromucamide is obtained by dropping small portions of powdered pyromucamide into bromine kept cooled below zero. One should use 3.6 parts of bromine to one part of pyromucamide; that is, about five atoms of bromine to one molecule of pyromucamide. The liquid becomes thick and should be well stirred. After the pyromucamide has all been added, the excess of bromine is allowed to evaporate, and cold alcohol poured over the well cooled residue. On standing, a pale yellow, finely divided solid separated from the dark mass. After the latter has been completety broken up, the product is filtered off and washed with ether. The yield is between 50 and 60 per cent. of the calculated amount. For further purification the substance is dissolved in ethyl acetate or acetone, and the greater part of the solvent distilled off. It is then filtered, and washed again with ether. The substance is thus obtained in minute, color-less, glistening crystals. An analysis gave the following results:

I. 0.3417 gram substance gave 0.1751 gram CO_2 and 0.0410 gram H_2O.

II. 0.1110 gram substance gave 0.1950 gram AgBr.

III. 0.4586 gram substance gave 13.6 cc. of moist nitrogen at 23.5° and 765 mm. pressure.

	Calculated for $C_5H_5NBr_4O_2$.	I.	Found. II.	III.
C	13.92	13.98	...	...
H	1.16	1.33	...	...
Br	74.25	...	74.76	...
N	3.25	...	...	3.36

The substance is therefore the tetrabromide of pyromucamide.

Properties of Pyromucamide Tetrabromide.—It is a crystalline solid without color or odor. Its melting-point is about 121°, as determined in the ordinary way, but it varies with the rapidity of the heating. By long heating the substance will melt, always with evident decomposition, even below 100°. It is insoluble in water, almost insoluble in ether, chloroform, glacial acetic acid, or

alcohol, somewhat more readily soluble in ethyl acetate and acetone. It is decomposed by boiling with water, alcohol, or glacial acetic acid. When it was dissolved in alcohol and treated with zinc dust in the cold, the bromine was abstracted and pyromucamide formed. On boiling with water it is decomposed; hydrobromic acid is formed, but no definite organic compound could be isolated. In order to study the products formed by the action of alkalies, the tetrabromide was added gradually, in small portions, to *cold* concentrated alcoholic sodium hydroxide. After standing in the cold for about an hour, the mixture was allowed to remain for several days in a warm room, the alcohol being renewed when necessary. Ammonia was slowly evolved. The alcohol was then evaporated off, and the solid residue treated with water. Only a very small portion of insoluble matter was left. This was filtered off. On acidifying the filtrate, an acid was precipitated which was purified by converting it into the barium salt and separating the latter by fractional crystallisation into three portions. The acid was then liberated from each portion separately. It appeared to be $\beta\gamma$-dibrompyromucic acid, since each fraction melted at about 192°, the purest at 191.5°. To remove all doubt, this portion was dissolved in absolute alcohol, and converted into the ethyl ester by the action of dry hydrochloric acid. The observed melting-point of the ester, 67.5°, completed the proof as to the nature of the acid, since the $\beta\gamma$-dibrompyromucic acid melts at 191°–192°, and its ethyl ester at 67°–68°.[1] $\beta\delta$-dibrompyromucic acid does not seem to be formed at all in this decomposition of pyromucamide tetrabromide. Even microscopic examination failed to prove its presence, though the crystals are quite characteristic. This is interesting in consideration of the fact observed by Hill and Sanger,[1] that the tetrabromide of pyromucic acid yields, under similar circumstances, a mixture of the two isomeric dibrompyromucic acids ($\beta\gamma$ and $\beta\delta$).

The Action of Bromine Water on Pyromucamide.

Some remarkable color reactions observed by Professor Hill, when studying the action of bromine and potassium hydroxide on pyromucamide, led to the suggestion that interesting results might be obtained in that direction by further work. The author therefore gave a short time to the study of the nature of these color

[1] Proceedings Am. Academy **21**, 155 *et seq.*

reactions, as well as those produced when bromine water is used in place of pure bromine, and when other basic substances are used in place of potassium hydroxide.

Pyromucamide treated with bromine water dissolves readily, producing a solution almost or quite colorless. This was treated in various ways in order to isolate, if possible, some definite substance from it, but amorphous dark products were always obtained. If to the fresh solution there is added almost any strongly basic inorganic substance, a dark blue (or sometimes purple) color is soon produced, the rapidity of its production depending apparently on the strength of the base. The color usually changes to purple in a short time, and afterwards undergoes other alterations, generally passing to red, and finally, if the amount of pyromucamide used is small, fading to pale yellow. When the base employed is barium hydroxide, a dark blue amorphous precipitate is produced. An investigation was made as to the quantity of bromine required to produce the maximum intensity of color from a given amount of pyromucamide. Measured quantities of dilute solutions of pyromucamide and bromine were mixed, shaken, and allowed to stand a few moments. Then an excess of sodium hydroxide was added, and the colors produced were compared. It was found that two atoms of bromine to each molecule of pyromucamide gave the deepest color on subsequent treatment with alkali. Either a deficiency or an excess of bromine is unfavorable to the color production. The dark blue compound was too unstable for isolation.

The production of this color may serve as a very delicate test for pyromucamide. When one milligram of the amide is dissolved in a drop of dilute bromine water, and the solution made alkaline, the blue (or purple) color produced is quite distinct.

Chlorine water can be used instead of bromine water, but the color was not obtained when iodine or nitric acid was employed. Substituted pyromucamides, so far as investigated, do not give the color reaction: δ-methylpyromucamide, $\beta\delta$-dibrompyromucamide, and $\beta\gamma$-dichlorpyromucamide were tried.

If instead of sodium hydroxide, an aqueous solution of aniline is added to the solution of pyromucamide in bromine water, a *reddish precipitate* is produced. This substance is not stable. It melts at about 78°, and appears to undergo decomposition when treated with alcohol even in the cold.

By substituting a saturated aqueous solution of phenylhydrazine

for aniline, a brilliant red precipitate was obtained. The most convenient method for preparing this substance is as follows: Dissolve a weighed amount of pyromucamide in as small a quantity of water as convenient; add to this bromine, a few drops at a time, shaking the flask and keeping it cool, until for each molecule of pyromucamide two atoms of bromine have been added. The bromine will be dissolved, and the solution will be almost colorless. Filter if necessary, and add a large excess of a saturated solution of phenylhydrazine in water. Allow the mixture to stand for some time, filter off the red precipitate formed, wash with water, then with two or three small portions of alcohol, and lastly with ether. Dry over sulphuric acid or in a steam-drying oven. The yield is about 1.6 times the weight of the amide taken. The substance as thus obtained is bright red in color. It has no definite melting-point, but darkens in color between 150° and 160°. It is dissolved, and probably decomposed, by aqueous or alcoholic potassium hydroxide, with a marked increase in the intensity of the red color. It is very slightly soluble in chloroform, ether, and carbon disulphide, somewhat more readily in alcohol and acetone. Boiling with alcohol and other solvents decomposes it, but it can be obtained in small scale-like crystals by making a saturated solution at 50° in alcohol or acetone, and allowing it to cool and evaporate spontaneously. The crystals are darker in color than the amorphous material, and are quite brilliant. Qualitative tests showed the absence of bromine. Analyses of the substance, both in the crystalline and the amorphous state, were made with identical results.

The material used in analyses I and II was crystallised from acetone, washed with ether and dried at 100°, while in analyses III and IV an amorphous preparation was used which had been washed successively with water, alcohol, and ether, and dried over sulphuric acid.

I. 0.3001 gram substance gave 0.6684 gram CO_2 and 0.1423 gram H_2O.

II. 0.1005 gram substance gave 17.2 cc. of moist nitrogen at 23.5° and 754 mm. pressure.

III. 0.1740 gram substance gave 0.3879 gram CO_2 and 0.0857 gram H_2O.

IV. 0.2196 gram substance gave 37.9 cc. moist nitrogen at 21.5° and 741 mm. pressure.

	Calculated for $C_{11}H_{11}N_3O_2$.	Found.			
		Crystalline.		Amorphous.	
		I.	II.	III.	IV.
C	60.83	60.74	...	60.80	...
H	5.07	5.27	...	5.47	...
N	19.35	...	19.08	...	19.10

The formula of the substance $C_{11}H_{11}N_3O_2$ shows that it contains the elements of one molecule of phenylhydrazine, and one of pyromucamide, less two atoms of hydrogen. Lack of time prevented a more extended study of this body, but the investigation will be continued at some future time in this laboratory.

REVIEWS AND REPORTS.

RECENT PROGRESS IN PHYSICAL CHEMISTRY.

The Theory of Solutions.

1. *Non-electrolytic solutions.*—The early development of van't Hoff's Theory of Solutions has been reviewed in this Journal **12**, 130, and it seems now in place to consider in outline the work which has since been done. The principle of van't Hoff's derivation[1] of the laws governing the changes of the vapor-pressures, boiling-points and freezing-points of solutions should first be clearly stated. Since the general equation $pv = RT$, summarising the laws of Boyle, Gay-Lussac and Avogadro, had been shown to be the equation of condition for solutions, it became at once possible to carry through various reversible cycles of operations with solutions, and thereby make application of that eminently fruitful principle, the second law of thermodynamics.

a. The vapor-pressure law.—In a reversible cycle at constant temperature, that amount of solvent containing 1 g-molecule of dissolved substance in dilute solution is removed by means of a cylinder and semi-permeable piston. The work done is pv, or $2T$. Suppose the solution to contain n g-molecules substance in N g-molecules solvent. The solvent thus obtained is vaporised at its vapor-pressure f, yielding work $N/n.2T$. Expanding the vapor to the pressure f' of the solution yields work $(f - f')v$ or

[1] van't Hoff: Zeit. f. ph. Ch. **1**, 481 (1887).

$N/n.2\,T.(f-f')/f.$ Condensing the vapor in contact with the solution work $N/n.2\,T$ is required.   The gain of work $N/n.2\,T.$ $(f-f')/f$ must then equal the initial expenditure $2\,T$, giving

$$(f-f')/f = n/N,$$

the vapor-pressure law.

b. The boiling-point law.—Consider the same solution as above. N/n g-molecules of solvent are freed in the same way as before and are vaporised at the absolute boiling temperature T of the solvent, absorbing $N/n.\rho$ cal., ρ representing its molecular heat of vaporisation.   Heat solvent and solution to the latter's boiling-point $T + \varDelta T$, and condense the vapor in contact with the solution, gaining a greater quantity of heat $N/n.\rho'$ cal.   Cool $\varDelta T$ degrees, completing the cycle.   According to the first law of thermodynamics,

$$N/n.(\rho'-\rho) = 2\,T.$$

$\int dQ/T$ becomes for this case $\varSigma Q/T = 0$, or

$$\frac{\dfrac{N}{n}\rho}{T} = \frac{\dfrac{N}{n}\rho'}{T+\varDelta T},\text{ whence}$$

$$\frac{\varDelta T}{n} = \frac{1}{N}\cdot\frac{2\,T^2}{\rho},\text{ or }\frac{\varDelta T}{n} = \frac{0.02\,T^2}{r}$$

for 100 g. solvent, r representing its specific heat of vaporisation. $\varDelta T/n$ is the molecular rise of boiling-point.

c. The freezing-point law.—By means of a reversible cycle of the same nature as the preceding, commencing at the absolute freezing temperature T of the solvent and freezing the solvent gained instead of vaporizing it one obtains, λ representing the molecular heat of fusion of the solvent at T,

$$\frac{N}{n}\Big(\lambda-\lambda'\Big) = pv = 2\,T,$$

$$\frac{\dfrac{N}{n}\lambda'}{T-\varDelta T} = \frac{\dfrac{N}{n}\lambda}{T},\text{ whence}$$

$$\frac{\varDelta T}{n} = \frac{1}{N}\cdot\frac{2\,T^2}{\lambda},\text{ or }\frac{\varDelta T}{n} = \frac{0.02\,T^2}{l}$$

for 100 g. solvent, l representing its specific heat of fusion. $\varDelta T/n$ is the molecular depression of the freezing-point.

The direct methods of measuring the pressures exerted by dissolved substances require the elimination of the counterbalancing inner pressure (*Binnendruck*), normal to the surface of the liquid. From the assumptions of the kinetic theory of gases van der

Waals has calculated this inner pressure to have for ether the enormous value of about 1300 atmospheres. The following ingenious calculation of the same quantity is due to Stefan.[1] The work required to bring a small portion of the liquid from the interior to the surface of its volume v, against this inner pressure P, is $(P-p)v$, p representing the vapor-pressure. This portion of liquid is now free from the attraction of half the surrounding mass, an additional equal amount of work frees it from the attraction of all and it becomes vapor. The total work is the heat of vaporation r, i. e. $2(P-p)v=r$, or for the actual inner pressure $P-p=r/2v$. For one gram ether at 0° C. $r=86$ cal.$=86 \times 42$ 355g-cm., $v=1.37$ ccm., 1 atm.$=1033.2$g/cm², so that

$$P-p = \frac{86 \times 42\ 355}{2 \times 1.37 \times 1033.2} = 1287 \text{ atm.}$$

An interesting and simple deduction has been given by Fick.[2] The total pressure under which a solution stands must be the sum of the partial pressures of dissolved substance and solvent, each being proportional to the concentration, and unit molecular concentration (1g-mol. per liter) causing a pressure of 22.35 atm. Pfeffer found the osmotic pressure of a one-per cent. cane-sugar solution to be 49.3 cm. mercury. In this solution the molecular concentration of the water is 1881 times that of the sugar, and its partial pressure is greater in the same ratio. The solution stands then under a total pressure of

$$\frac{1882 \times 49.3 \times 13.57}{1033.2} = 1219 \text{ atm.,}$$

the sp. gr. of mercury being 13.57. This figure is in striking agreement with the results of van der Waals (near 1300) and Stefan (1287).

In a comparison of the osmotic pressures observed in the protoplasma cells of different organisms, Tammann[3] has called attention to the singular fact that these pressures are in most cases equal. In the cells of the nerves of frog's legs, in the red blood corpuscles, in the sea algae, and in the cells of land plants the pressure has a constant value of about 4.5 atmospheres. In the cells of the bacteria the osmotic pressure is great, about 16 atmospheres, corresponding to the fact that their activity is a destructive one, transforming compounds of high molecular weights into such of lower. It is evident how greatly this abnormal capacity for resistance supports them in their destructive work.

Beckmann's boiling-point method of determining molecular weights was reviewed in this Journal **12**, 134; since that time Beckmann's experimental results[4] have appeared. A large number of eminently satisfactory determinations were made in the

[1] Stefan : Wied. Ann. **29**, 655 (1886).   [2] Fick : Zeit. f. ph. Ch. **5**, 526 (1890).
[3] Tammann : Zeit. f. ph. Ch. **8**, 685 (1891).   [4] Beckmann : Zeit. f. ph. Ch. **6**, 437 (1890).

following ten solvents; the molecular rise of boiling-point $\Delta T/n$ and the specific heat of vaporisation being given for each as follows :

	$\Delta T/n$.	r.
Ethylene bromide	63.2	51.8
Chloroform	36.6	61.0
Benzene	26.7	93.4
Ethyl acetate	26.1	92.7
Acetic acid	25.3	121.0
Carbon bisulphide	23.7	84 8
Ethyl ether	21.1	90.1
Acetone	16.7	129.7
Ethyl alcohol	11.5	214.9
Water	5.2	536.4

An example is an experiment with benzophenone in carbon bisulphide :

g. substance.	g. solvent.	ΔT.	mol. wt.	Theory.
1.4699	90.60	0.211	182	182
2.9050	...	0.406	187	...

In this paper Beckmann shows conclusively that the needful constant $\Delta T/n$ is to be directly and accurately determined from the heat of vaporisation of the solvent, according to van't Hoff's formula $\Delta T/n = 0.02\ T^2/r$. The author points out that the different solvents can be arranged in a series with respect to their "dissociating force," water coming first, with its capacity of often effecting dissociation into ions. Acetic acid strikingly, the alcohols, phenols, esters, ethers, and to a certain extent acetone, effect solution of substances with normal molecular weights. A tendency to the formation of double molecules is exhibited by some organic acids, oximes and phenols when dissolved in anethol, azobenzene and paratoluidine, and still more strongly when in the hydrocarbons, ethylene bromide, CS_2 and $CHCl_3$. The new method can yield, however, better practical results than vapor density determinations when, as is usual, the *smallest* mol. wt. is desired, since many solvents have a greater dissociating force than has a vacuum.

Certain improvements in the boiling apparatus, adapting it to high-boiling solvents, are described in a further paper.[1] Beckmann has recently shown[2] how his freezing apparatus may be employed in working with high-melting solvents, and has described a simple arrangement for avoiding the absorption of moisture by hygroscopic solvents, by means of a gentle current of dried air passed into the apparatus. A little moisture may often have a serious effect in changing the freezing-point, owing to the low molecular weight of water.

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[1] Beckmann : Zeit. f. ph. Ch. **8**, 223 (1891).   [2] *Ibid.* **7**, 323 (1891).

Successful and extended application of van't Hoff's formula $\varDelta T/n = 0.02\,T^2/r$ (or l), in the determination of heats of vaporisation and of fusion by the boiling and freezing-point methods, has been made by Eyckman and by Beckmann. See Zeit. f. ph. Ch. **2**, 964; **3**, 113; **3**, 203; **3**, 603; **4**, 497; **6**, 461.

Van't Hoff's vapor-pressure law of solutions has been applied by Ramsay[1] to a study of the molecular weights of the metals dissolved in mercury as amalgams. The method employed was that of direct measurement of the vapor-pressures in barometer tubes. Li, Na, K, Mg, Mn, Zn, Ga, Cd, Ag, Sn, Sb, Au, Tl, Pb, Bi, were found to have monoatomic molecular weights. The molecular weights found for Ca and Ba were about half the recognised atomic weights, yet the figure for Ca is stated to be very uncertain. Al gave values 33–37.

From freezing-point depressions of amalgams Tammann[2] found monoatomic molecular weights for K, Na, Tl and Zn. Heycock and Neville[3] found normal atom depressions for solutions of Au, Tl, Hg, Cd, K, In, in sodium. In tin the theoretical depression is about 3°, and normal values averaging 2.83 were obtained from Ni, Ag, Au, Cu, Tl, Na, Pd, Mg, Pb and Zn. Cd, Hg, Bi and Ca gave somewhat lower values, In and Al tended apparently to form double molecules. Antimony *raised* the freezing-point, a singular phenomenon whose explanation is given below in the review of van't Hoff's theory of solid solutions.

Nernst has shown[4] that the osmotic pressure of solutions requires an opposed "solution pressure" of the dissolving substances, causing their diffusion into the solvent, and measured by the pressure of the saturated solution. This is in every respect analogous to the "vapor pressure" of a substance, measured by the pressure of its saturated vapor. Both pressures being exactly alike, the quantitative relations derived for the one are derivable for the other, and hence the general thermodynamical vapor-pressure formula $dp/dT = s/T.\varDelta v$ represents in exact form the change of pressure of a saturated solution with changing temperature, as dependent upon the heat of solution s (thermodynamically defined as the heat-quantity *added*) and volume-increase $\varDelta v$. From this equation the interesting conclusion has been drawn by Le Chatelier,[5] and also by van't Hoff,[6] that since T and $\varDelta v$ are essentially positive quantities, dp/dT and s must have the same sign. If the dissolving be accompanied by heat-absorption, the pressure p of the saturated solution, and necessarily also its concentration, increase with rising temperature, the reverse taking place if heat be evolved. The relation is extensively supported by experimental evidence.

[1] Ramsay: Jour. Chem. Soc. 1889, 521.
[2] Tammann: Zeit. f. ph. Ch. **3**, 441 (1889).
[3] Heycock and Neville: Jour. Chem. Soc. 1889, 666; 1890, 376.
[4] Nernst: Zeit. f. ph. Ch. **4**, 150 (1889).
[5] Le Chatelier: Comptes rendus **100**, 441 (1885).
[6] van't Hoff: Archives néerlandaises **20**, 53 (1886).

For the solution of one g-molecule of a substance, Δv in the above equation becomes v, whose value is obtainable from the gas equation $pv = RT$, giving

$$\frac{dp}{dT \cdot p} = \frac{s}{RT^2} \quad \text{or} \quad \frac{d\log p}{dT} = \frac{s}{RT^2}.$$

van't Hoff has [1] used this equation to calculate the heats of solution of substances from their solubility curves, determining the change in the logarithms of the concentrations ($d\log p$) for a small finite temperature change (dT), and setting for T the average temperature of the experiment. The electrolytic dissociation of the substances considered requires that the gas-constant R be multiplied by the coefficient i, representing the increased total number of g-molecules present per g-formula weight, *i. e. $pv = iRT$.* Solving for s he obtained, for example, such results as :

	Temperatures.		Solubilities.		i.	s/100. Theory.	s/100. Observed.
Lime	15.6	54.4	0.129	0.103	2.59	-28	-28
K-bioxalate	0	10	2.2	3.1	1.84	$+98$	$+96$
K-bichromate	0	10	4.6	7.4	2.36	$+173$	$+170$

A third conclusion has been drawn from the equation $dp/dT = s/Tv$, and experimentally verified by J. Walker [2] in Ostwald's laboratory. The vapor-pressure curves of a solid and liquid intersect, at the melting-point, at an angle dependent upon the heat of fusion. The solubility of a substance suffers with increasing temperature no discontinuous change on passing its melting-point, yet the solubility curves of solid and liquid must here intersect at an angle dependent upon the heat of fusion. Integrating the equation $dp/p = s/2\,T^2 . dT$, and multiplying by T, we have

$$T\log p = -s/2 + (\log p_0 + s/2\,T_0)\,T, \tag{1}$$

T_0 and p_0 representing respectively melting-point and pressure in the saturated solution of the dissolved substance. This relation obtaining for the solid, for the liquid the heat of solution is increased by the molecular heat of fusion λ, or

$$T\log p' = -\frac{s+\lambda}{2} + \left(\log p_0 + \frac{s+\lambda}{2\,T_0}\right) T. \tag{2}$$

Assuming s to be constant over the temperature-interval considered, eq. (1) becomes the equation of a straight line, the tangent of whose angle with the T-axis is

$$\tan \alpha = \log p_0 + s/2\,T_0 \quad \text{or} \quad s = 2\,T_0\,(\tan \alpha - \log p_0).$$

Likewise from (2),

$$s + \lambda = 2\,T_0\,(\tan \alpha' - \log p_0).$$

Subtracting :
$$\lambda = 2\,T\,(\tan \alpha' - \tan \alpha).$$

[1] van't Hoff: Archives néerl. **20**, 55 (1886).   [2] Walker: Zeit. f. ph. Ch. **5**, 193 (1890).

Tan α is determined experimentally from the solubility curves, from which then the molecular heat of fusion λ of the dissolved substance is obtained. Walker found thus for p-toluidine (dissolved in water) 44.5 cal. per gram, approximating the actual value 39 cal. For water (dissolved in ether) 77 cal. was found as against 80 cal., the actual value. Hereby was discovered that water dissolved in ether has the molecular formula H_4O_2, which is interesting in connection with the observation of Eyckman, from the freezing-point method, that water in p-toluidine is also H_4O_2. Dissolved in phenol, however, it has the normal molecular weight 18.

Defining solutions as homogeneous mixtures, non-separable into their components by mechanical means, and whose composition can vary without destroying their homogeneity, van't Hoff has shown [1] that in addition to gaseous and liquid solutions, solid ones have a claim for consideration, thus considerably extending the applicability of the general solution laws. Instances of solid solutions are the alloys, isomorphous mixed crystals and the various kinds of glass. That the dissolved substances in solid solution stand under a definite partial pressure, as in the liquid and gaseous ones, is demonstrated by their tendency to diffuse, as in the diffusion of iron into carbon, or the reverse, at high temperatures; of calcium into iron, of copper into platinum, of zinc into copper, and many more.

In the first case cited (iron and carbon), pressure and concentration were experimentally shown to be proportional (Boyle's law), and for solutions of hydrogen in palladium hydride Pd_2H the absorption is proportional to the pressure of the hydrogen gas (Henry's law). Suitable combination of these results shows the pressures in solid solutions to be the same as those in liquid solutions *or gases*, at the same concentrations and temperatures.

Further, that the formation of solid solutions decreases the vapor-pressure appears *e. g.* from the ready weathering of lead thiosulphate, which is greatly diminished by the addition of a small amount of the isomorphous Ca or Sr salt. In fact, in such cases, the resulting solid solutions may have lower vapor-pressures than has either constituent. In the same way the analogous "solution pressures" of salts, and hence their solubilities, are diminished by the formation of mixed crystals.

Since the freezing-point is given by the intersection of the vapor-pressure curves of liquid and solid, it follows that forming a liquid solution depresses the freezing-point, forming a solid solution raises it, and both processes may take place together. Under van't Hoff's direction van Bijlert [2] has shown that this simple explanation accounts for the observed "abnormal" freezing-point depressions, in each case the crystals separated on freezing being a solid solution and not the pure solvent. Further than this, that

[1] van't Hoff: Zeit. f. ph. Ch. **5**, 322 (1890). [2] van Bijlert: Zeit. f. ph. Ch. **8**, 343 (1891).

antimony dissolved in melted tin *raises* its freezing-point has been shown by him to be due to the formation of a solid solution of antimony in tin, the crystals separated on freezing containing even more antimony than the remaining liquid solution.

A recent paper by Küster[1] contains the results of a study of the dependence of the freezing-point of a mixture of two isomorphous organic substances upon its composition. The melting point was found to be an additive property of the mixture, changing directly in proportion to the change of molecular concentration. Such substances as tri-chlor- and tri-brom-acetamide, and dihydro-naphthalene and naphthalene, were thus shown to be isomorphous. That the general law for the freezing-points of solutions does not apply in these cases results from the separation of a solid solution (mixed crystals) on freezing, and not the pure solvent as required by the simple van't Hoff formula.

By a most simple application of the Mass Law, from the proportionality between the concentrations of gas and solution, in the case of H_2 dissolved in Pd_2H, van't Hoff has shown this dissolved hydrogen to possess the molecular formula H_2. In a similar way, from Roozeboom's experimental results on the solubilities of mixed crystals, Nernst has calculated [2] the molecular weight of $KClO_3$ in dilute solid solution in $TlClO_3$ to correspond to the molecular formula $KClO_3$ and *not* to $(KClO_3)_2$, double molecules, for example.   Trevor.

Cornell University.

[1] Küster: Zeit. f. ph. Ch. 8, 577 (1891).   [2] Nernst: Zeit. f. ph. Ch. 9, 141 (1892).

AMERICAN

CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College

LXXVI.—ON CHLORSULPHOPYROMUCIC ACIDS.[1]

By Henry B. Hill and Walter S. Hendrixson.

The sulphonic acids which may be formed by the action of fuming sulphuric acids upon the several brompyromucic acids were described a few years ago by Hill and Palmer.[2]   The chlorpyromucic acids, which were at that time unknown, were afterwards studied by Hill and Jackson,[3] and were shown to differ in certain respects quite essentially from the corresponding bromine derivatives.   It therefore seemed to us advisable to study also the behavior of these acids toward fuming sulphuric acid.

β-Chlor-δ-Sulphopyromucic Acid.

β-chlorpyromucic acid dissolves readily in fuming sulphuric acid (sp. gr. 1.95), and the corresponding sulphonic acid is rapidly formed without appreciable carbonisation. The β-chlorpyromucic acid itself we prepared by reducing $\beta\gamma$-dichlorpyromucic acid with sodium amalgam containing one per cent. of sodium.   Complete reduction could be effected by using one and a half times the calculated amount of amalgam, and about fifty per cent. of the theoretical yield of β-chlorpyromucic acid was obtained.   The β-chlor-δ-sulphopyromucic acid was isolated in the usual way,

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[1] Presented at a meeting of the American Academy of Arts and Sciences, held February 11, 1891.

[2] This Journal 10, 373 and 409; and Proc. Am. Acad. 23, 188.

[3] This Journal 12, 22 and 112; and Proc. Am. Acad. 24, 320.

after neutralising the diluted acid solution with baric carbonate. The free acid crystallises in hemispherical masses of indistinct radiating needles, which deliquesce rapidly when exposed to moist air.

Baric β- Chlor-δ-Sulphopyromucate, $BaC_5HClSO_6.4H_2O.$

This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallises in prisms which contain four molecules of water. When exposed to the air it slowly effloresces, and loses its water readily over sulphuric acid or when heated to 100°.

I. 0.7880 gram of salt dried by short exposure to the air gave 0.4246 gram $BaSO_4$.

II. 0.6729 gram air-dried salt gave 0.3631 gram $BaSO_4$.

III. 1.5568 grams air-dried salt lost at 100° 0.2547 gram H_2O.

IV. 1.1932 grams air-dried salt lost over H_2SO_4 0.1935 gram H_2O.

	Calculated for $BaC_5HClSO_6.4H_2O.$	I.	II.	III.	IV.
			Found.		
Ba	31.60	31.63	31.72	...	...
H_2O	16.61	...	...	16.36	16.22

I. 0.6958 gram salt dried at 100° gave 0.4477 gram $BaSO_4$.

II. 1.0371 grams salt dried over H_2SO_4 gave 0.6678 gram $BaSO_4$.

	Calculated for $BaC_5HClSO_6.$	I.	II.
		Found.	
Ba	37.89	37.83	37.86

The solubility of the salt in cold water we determined in the usual way.

I. 15.6246 grams solution saturated at 20° gave 0.1888 gram $BaSO_4$.

II. 17.2519 grams solution saturated at 20° gave 0.2084 gram $BaSO_4$.

The solution saturated at 20° therefore contained the following percentages of anhydrous salts:

I.	II.
1.87	1.87

Plumbic β- Chlor-δ-Sulphopyromucate, $PbC_5HClSO_6.4H_2O.$

The lead salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallises when its hot aqueous solu-

tion is cooled in thick rhombic prisms which contain four molecules of water. The salt effloresces slowly when exposed to the air, loses the greater part of its water over sulphuric acid, and becomes anhydrous when heated to 125°.

I. 0.7342 gram air-dried salt gave 0.4416 gram $PbSO_4$.

II. 1.7839 grams air-dried salt lost at 125° 0.2552 gram H_2O.

III. 0.7343 gram air-dried salt lost at 125° 0.1045 gram H_2O.

	Calculated for $PbC_5HClSO_6.4H_2O$.	I.	Found. II.	III.
Pb	41.11	41.09	...	...
H_2O	14.30	...	14.31	14.23

I. 0.6298 gram salt dried at 125° gave 0.4416 gram $PbSO_4$.

II. 0.6611 gram salt dried at 125° gave 0.4634 gram $PbSO_4$.

	Calculated for PbC_5HClSO_6.	I.	Found. II.
Pb	47.97	47.88	47.88

Potassic β-Chlor-δ-Sulphopyromucate, $K_2C_5HClSO_6.H_2O$.

The potassium salt was readily soluble even in cold water, but was obtained by cooling a hot concentrated aqueous solution in the form of transparent prisms, which effloresced over sulphuric acid.

I. 0.7895 gram air-dried salt gave 0.4260 gram K_2SO_4.

II. 1.7840 grams air-dried salt lost at 110° 0.1104 gram H_2O.

	Calculated for $K_2C_5HClSO_6.H_2O$.	I.	Found. II.
K	24.39	24.22	...
H_2O	5.61	...	6.18

I. 0.9626 gram salt dried at 110° gave 0.5464 gram K_2SO_4.

II. 0.7043 gram salt dried at 110° gave 0.4003 gram K_2SO_4.

	Calculated for $K_2C_5HClSO_6$.	I.	Found. II.
K	25.83	25.48	25.52

While there could be little doubt of the constitution of the sulphonic acid formed from β-chlorpyromucic acid, we attempted to establish more definitely the position of its sulpho-group by reducing it to the δ-sulphopyromucic acid. We found, however, that the chlorine was much more firmly held than the bromine of the corresponding β-brom-δ-sulphopyromucic acid, and that the reduction could not be effected by the ordinary reducing agents.

Zinc dust in an ammoniacal solution, which had given satisfactory
results with the bromsulphopyromucic acids, removed the chlorine
so slowly that, even after boiling the solution for days, the reduc-
tion was far from complete.   On the other hand, sodium amalgam
added to the aqueous solution of the barium salt at once attacked
the sulpho-group, baric sulphite was precipitated, and β-chlorpy-
romucic acid was formed.   With other reducing agents in acid
solution we were equally unsuccessful.   The ready elimination of
the sulpho-group by the action of sodium amalgam in alkaline
solution was so unexpected that we were led to examine the
behavior of other sulphopyromucic acids under the same condi-
tions.   We found that δ-sulphopyromucic acid was thus readily
reduced to pyromucic acid, while β-sulphopyromucic acid was
apparently unaffected, and that the halogen derivatives of these
two acids which we had at our disposal showed precisely the same
difference in behavior.   The removal of the sulpho-group from
the chlorsulphopyromucic acid in question may therefore be taken
as evidence that the sulpho-group is in the δ-position.

Action of Bromine.

Like all the derivatives of δ-sulphopyromucic acid which have
thus far been examined, β-chlor-δ-sulphopyromucic acid is at once
oxidised by bromine in aqueous solution, and sulphuric acid is
formed.   Bromine was added in slight excess to a solution of the
barium salt of the acid, the baric sulphate removed by filtration,
and the acid filtrate extracted with ether.   The acid thus obtained
was very readily soluble in water and practically insoluble in
benzol.   After recrystallisation from water it was dried and
washed with benzol.   The acid thus purified melted at 188°, and
with the quantity at our command we found it impossible to raise
this melting-point.   Although chlorfumaric acid melts at 191°,[1]
there can be no doubt that chlorfumaric acid had been formed in
the reaction.

Action of Nitric Acid.

Like the brom-δ-sulphopyromucic acids, the β-chlor-δ-sulpho-
pyromucic acid is readily converted into the corresponding nitro-
acid by the action of fuming nitric acid.   For its preparation we
dissolved the dry sulphonic acid in cold fuming nitric acid, warmed

[1] Kauder: J. prakt. Chem. [2] **31**. 28.

the solution for some time upon the water-bath, and finally evaporated the nitric acid at a gentle heat. The crystalline product thus obtained was recrystallised first from water, then from benzol, and finally from water. The β-chlor-δ-nitropyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallises in thick clustered needles. By the slow cooling of the hot solution, or by spontaneous evaporation of the solution, well-formed monoclinic (?) prisms with beveled ends are obtained. The crystallised acid contains one molecule of water, part of which at least it loses over sulphuric acid, and the whole of which may be driven off at 75°. The anhydrous acid melts at 140°–141°.

1.4274 grams air-dried substance lost at 75° 0.1281 gram H_2O.

	Calculated for $C_5H_2ClNO_6.H_2O$.	Found.
H_2O	8.59	8.97

I. 0.2623 gram substance dried at 75° gave 0.1970 gram AgCl.
II. 0.2070 gram substance dried at 75° gave 13.8 cc. of moist nitrogen at 25° under a pressure of 762 mm.

	Calculated for $C_5H_2ClNO_5$.	I.	II.
Cl	18.54	18.57	...
N	7.31	...	7.45

$\beta\gamma$-Dichlor-δ-Sulphopyromucic Acid.

$\beta\gamma$-dichlorpyromucic acid dissolves without charring in fuming sulphuric acid, and in the course of a few hours is converted into the corresponding sulphonic acid. The barium salt obtained by neutralising the diluted solution with baric carbonate is quite readily soluble in cold water, but it can be purified without difficulty by recrystallisation from hot water. The free acid crystallises in distinct radiating needles, and deliquesces rapidly when exposed to the air.

Baric $\beta\gamma$-Dichlor-δ-Sulphopyromucate, $BaC_5Cl_2SO_6.5H_2O$.

This salt is very readily soluble in hot water, less soluble in cold water, and separates as the hot solution cools in globular aggregations of radiating needles which contain five molecules of water. The salt is permanent in the air, but slowly effloresces over sulphuric acid. It loses a part of its water at 100°, but a temperature of 180° appears to be necessary for complete dehydration.

I. 0.4258 gram air-dried salt gave 0.2045 gram $BaSO_4$.
II. 1.0938 grams air-dried salt gave 0.5239 gram $BaSO_4$.
III. 1.5844 grams air-dried salt lost at 185° 0.2930 gram H_2O.
IV. 0.9712 gram air-dried salt lost at 190° 0.1792 gram H_2O.

	Calculated for $BaC_5Cl_2SO_6.5H_2O$.	I.	II.	Found. III.	IV.
Ba	28.19	28.23	28.16	...	...
H_2O	18.52	...	...	18.49	18.45

I. 1.0167 grams salt dried at 185° gave 0.5970 gram $BaSO_4$.
II. 0.6549 gram salt dried at 190° gave 0.3837 gram $BaSO_4$.

	Calculated for $BaC_5Cl_2SO_6$.	I.	Found. II.
Ba	34.59	34.52	34.44

The solubility of the salt in cold water was also determined in the usual manner.

I. 18.7100 grams solution saturated at 18° gave 1.0970 grams $BaSO_4$.

II. 21.2012 grams solution saturated at 18° gave 1.2458 grams $BaSO_4$.

The aqueous solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
9.97	9.98

Plumbic βγ-Dichlor-δ-Sulphopyromucate, $PbC_5Cl_2SO_6.3H_2O$.

The lead salt is readily soluble in hot water, more sparingly soluble in cold water, and separates on cooling its concentrated aqueous solution in masses of fine needles.

I. 0.5342 gram air-dried salt gave 0.3106 gram $PbSO_4$.
II. 0.5524 gram air-dried salt gave 0.3212 gram $PbSO_4$.
III. 1.1523 grams air-dried salt lost at 160° 0.1163 gram H_2O.
IV. 1.2621 grams air-dried salt lost at 160° 0.1286 gram H_2O.

	Calculated for $PbC_5Cl_2SO_6.3H_2O$.	I.	II.	Found. III.	IV.
Pb	39.81	39.72	39.73	...	...
H_2O	10.39	...	...	10.09	10.19

I. 0.4520 gram salt dried at 160° gave 0.2910 gram $PbSO_4$.
II. 0.6342 gram salt dried at 160° gave 0.4107 gram $PbSO_4$.

	Calculated for $PbC_5Cl_2SO_6$.	I.	Found. II.
Pb	44.42	43.98	44.24

Potassic βγ-Dichlor-δ-Sulphopyromucate, $K_2C_5Cl_2SO_6.H_2O$.

This salt we made by precipitation with potassic carbonate from the barium salt. It was readily soluble even in cold water, and crystallised in needles which contained one molecule of water. The air-dried salt lost nothing over sulphuric acid.

I. 0.6161 gram air-dried salt gave 0.3017 gram K_2SO_4.

II. 0.6722 gram air-dried salt gave 0.3299 gram K_2SO_4.

III. 1.4226 grams air-dried salt lost at 160° 0.0686 gram H_2O.

	Calculated for $K_2C_5Cl_2SO_6.H_2O$.	I.	Found. II.	III.
K	22.02	21.99	22.04	...
H_2O	5.07	...	...	4.82

I. 0.6218 gram salt dried at 160° gave 0.3200 gram K_2SO_4.

II. 0.7197 gram salt dried at 160° gave 0.3688 gram K_2SO_4.

	Calculated for $K_2C_5Cl_2SO_6$.	I.	Found. II.
K	23.19	23.10	23.01

The calcium salt of the acid is very soluble even in cold water, and it was not obtained in a crystalline form.

Action of Bromine.

βγ-dichlor-δ-sulphopyromucic acid and its salts are immediately oxidised by bromine in aqueous solution, with the formation of carbonic dioxide, sulphuric acid, and dichlormaleic acid. Baric βγ-dichlor-δ-sulphopyromucate was suspended in water and a slight excess of bromine added. Baric sulphate was at once thrown down, and from the filtered solution dichlormaleic acid was obtained by extraction with ether. From the acid the anhydride was made by sublimation and its identity established through its melting-point, 119° to 120°.[1]

The formation of βγ-dichlor-δ-nitropyromucic acid through the action of fuming nitric acid has already been described by Hill and Jackson.[2]

β-Sulpho-δ-Chlorpyromucic Acid.

δ-chlorpyromucic acid was slowly added to four times its weight of fuming sulphuric acid (sp. gr. 1.95), and the solution allowed to stand for ten or twelve hours. The formation of the sulphonic

[1] Ciamician and Silber: Ber. d. chem. Gesell. **16**, 2396.

[2] This Journal **12**, 126; and Proc. Am. Acad. **24**, 361.

acid was then complete, and on neutralising the diluted solution with baric carbonate a barium salt was obtained which could easily be purified by recrystallisation from hot water. The free β-sulpho-δ-chlorpyromucic acid crystallised in dendritic needles which under ordinary atmospheric conditions are permanent in the air.

Baric β-Sulpho-δ-Chlorpyromucate, $BaC_5HClSO_6.5H_2O$.

This salt is readily soluble in hot water, and but sparingly soluble in cold water. It crystallises in large radiating needles which are permanent in the air, but slowly loses four of its five molecules of water over sulphuric acid.

I. 0.8535 gram air-dried salt gave 0.4411 gram $BaSO_4$.
II. 1.6218 grams air-dried salt gave 0.8371 gram $BaSO_4$.
III. 1.9648 grams air-dried salt lost at 130° 0.3893 gram H_2O.
IV. 0.9748 gram air-dried salt lost at 150° 0.1927 gram H_2O.
V. 1.9953 grams air-dried salt lost at 140° 0.3936 gram H_2O.

	Calculated for $BaC_5HClSO_6.5H_2O$.	I.	II.	Found. III.	IV.	V.
Ba	30.34	30.38	30.35	...	...	...
H_2O	19.93	...	...	19.81	19.76	19.73

1.5355 grams air-dried salt lost over H_2SO_4 0.2467 gram H_2O.

	Calculated for $BaC_5HClSO_6.5H_2O$.	Found.
$4H_2O$	15.95	16.06

I. 1.5480 grams salt dried at 130° gave 0.9992 gram $BaSO_4$.
II. 1.2325 grams salt dried at 140° gave 0.7866 gram $BaSO_4$.

	Calculated for BaC_5HClSO_6.	Found. I.	II.
Ba	37.89	37.96	37.52

The solubility of the salt in cold water was determined in the usual way.

I. 35 0277 grams solution saturated at 18° gave 0.3817 gram $BaSO_4$.
II. 27.2112 grams solution saturated at 18° gave 0.2985 gram $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
1.69	1.70

Acid Baric β-Sulpho-δ-Chlorpyromucate, $Ba(C_5H_2ClSO_6)_2.4H_2O$.

This salt was made by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It proved to be quite readily soluble in cold water, much more freely soluble in hot water, and separated on cooling in well-formed rhombic prisms which were permanent in the air and lost nothing over sulphuric acid.

I. 0.6413 gram air-dried salt gave 0.2261 gram $BaSO_4$.

II. 0.6463 gram air-dried salt gave 0.2281 gram $BaSO_4$.

III. 1.7167 grams air-dried salt lost at 125° 0.1855 gram H_2O.

	Calculated for $Ba(C_5H_2ClSO_6)_2.4H_2O$.	I.	Found. II.	III.
Ba	20.76	20.72	20.75	...
H_2O	10.91	...	...	10.81

I. 0.7345 gram salt dried at 125° gave 0.2900 gram $BaSO_4$.

II. 0.7734 gram salt dried at 125° gave 0.3052 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2ClSO_6)_2$.	I.	Found. II.
Ba	23.30	23.21	23.20

The solubility of the salt in cold water was also determined.

I. 6.7510 grams solution saturated at 20° gave 0.1935 gram $BaSO_4$.

II. 5.6625 grams solution saturated at 20° gave 0.1627 gram $BaSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
7.23	7.24

Calcic β-Sulpho-δ-Chlorpyromucate, $CaC_5HClSO_6.2H_2O$.

The calcium salt crystallises in transparent prisms which contain two molecules of water. It is permanent in the air or over sulphuric acid, and requires a high temperature for complete dehydration. The salt dried at 200° showed no signs of decomposition.

I. 0.9321 gram air-dried salt gave 0.4166 gram $CaSO_4$.

II. 0.8489 gram air-dried salt gave 0.3784 gram $CaSO_4$.

III. 1.6243 grams air-dried salt lost at 200° 0.1904 gram H_2O.

	Calculated for $CaC_5HClSO_6.2H_2O$.	I.	Found. II.	III.
Ca	13.31	13.14	13.11	...
H_2O	11.98	...	...	11.72

I. 0.5804 gram salt dried at 200° gave 0.2956 gram $CaSO_4$.
II. 0.7000 gram salt dried at 200° gave 0.3566 gram $CaSO_4$.

	Calculated for CaC_5HClSO_6.	Found. I.	II.
Ca	15.12	14.98	14.98

Plumbic β-Sulpho-δ-Chlorpyromucate, $PbC_5HClSO_6.H_2O$.

This salt is sparingly soluble in cold water, more readily soluble in hot water, and crystallises in compact clusters of radiating prisms. It loses nothing over sulphuric acid, or when heated to 100°.

I. 0.5646 gram air-dried salt gave 0.3799 gram $PbSO_4$.
II. 0.6672 gram air-dried salt gave 0.4485 gram $PbSO_4$.
III. 1.6403 grams air-dried salt lost at 165° 0.0705 gram H_2O.
IV. 1.5787 grams air-dried salt lost at 160° 0.0631 gram H_2O.
V. 1.6982 grams air-dried salt lost at 160° 0.0629 gram H_2O.

	Calculated for $PbC_5HClSO_6.H_2O$.	I.	II.	Found. III.	IV.	V.
Pb	46.06	45.95	45.93	...	...	...
H_2O	4.00	...	...	4.29	3.99	3.70

I. 0.5240 gram salt dried at 165° gave 0.3690 gram $PbSO_4$.
II. 1.0133 grams salt dried at 160° gave 0.7118 gram $PbSO_4$.
III. 0.5399 gram salt dried at 160° gave 0.3791 gram $PbSO_4$.

	Calculated for PbC_5HClSO_6.	I.	Found. II.	III.
Pb	47.98	48.10	48.01	47.96

Potassic β-Sulpho-δ-Chlorpyromucate, $K_2C_5HClSO_6$.

The potassium salt crystallises in long needles which are anhydrous.

I. 0.9272 gram air-dried salt gave 0.5309 gram K_2SO_4.
II. 0.8955 gram air-dried salt gave 0.5126 gram K_2SO_4.
III. 0.7962 gram air-dried salt gave 0.4562 gram K_2SO_4.

	Calculated for $K_2C_5HClSO_6$.	I.	Found. II.	III.
K	25.84	25.70	25.70	25.73

Although there could be little doubt that the sulphonic acid formed from δ-chlorpyromucic acid was identical in structure with the β-sulpho-δ-brompyromucic acid of Hill and Palmer,[1] we wished to prove this identity more rigorously by preparing from it by reduction the β-sulphopyromucic acid. We found that the method employed by Hill and Palmer in the reduction of the bromine compound could successfully be employed in this case, although the chlorine was replaced with much greater difficulty, and long-continued boiling of the ammoniacal solution with zinc dust was essential for complete reduction. We also found it advantageous to convert the baric β-sulphopyromucate into the acid salt, and to purify this by recrystallisation from hot water. The neutral salt was crystallised for analysis by evaporation *in vacuo* over sulphuric acid.

I. 0.7039 gram air-dried salt gave 0.4287 gram $BaSO_4$.

II. 1.0434 grams air-dried salt lost at 160° 0.1476 gram H_2O.

	Calculated for $BaC_5H_2SO_6 \cdot 3H_2O$.	I.	II.
		Found.	
Ba	35.96	35.80	...
H_2O	14.18	...	14.15

0.8946 gram salt dried at 160° gave 0.6347 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found.
Ba	41.90	41.72

The solubility of the salt in cold water was determined by the usual method.

I. 14.4785 grams solution saturated at 21° gave 0.1960 gram $BaSO_4$.

II. 12.0525 grams solution saturated at 21° gave 0.1628 gram $BaSO_4$.

The solution saturated at 21° therefore contained the following percentages of the anhydrous salt:

I.	II.
1.90	1.90

These results agree exactly with those obtained by Hill and Palmer for β-sulphopyromucic acid, and the relative position of the sulpho-group is thus established with precision.

[1] This Journal **10,** 409; and Proc. Am. Acad. **23,** 214.

Action of Bromine.

β-sulpho-δ-chlorpyromucic acid is readily oxidised in aqueous solution by bromine, carbonic dioxide is liberated, but little or no sulphuric acid is formed even when the action is long-continued at 100°. With an excess of bromine, an acid is formed which is undoubtedly identical with the sulphofumaric acid described by Hill and Palmer,[1] while a derivative of furfuran-β-sulphonic acid is formed in nearly theoretical quantity, if but a single molecule of bromine is added. For its preparation we passed into a cold aqueous solution of baric β-sulpho-δ-chlorpyromucate the vapor of the calculated weight of bromine by means of a current of air, and evaporated to a small volume the feebly acid solution thus obtained. The barium salt of the $\alpha\alpha$-chlorbromfurfuran-β-sulphonic acid which was thus obtained could then be purified by recrystallisation. By evaporation in desiccator the free acid was obtained as a waxy deliquescent mass, which showed but slight indications of crystalline structure.

Baric $\alpha\alpha$-Chlorbromfurfuran-β-Sulphonate,
$Ba(C_4HClBrSO_4)_2.H_2O.$

This salt is readily soluble in hot water, less soluble in cold water, and separates in pearly plates when its hot solution is quickly cooled. A cold solution by spontaneous evaporation deposits this salt in clusters of radiating needles.

I. 0.8479 gram air-dried salt gave 0.2936 gram $BaSO_4$.
II. 0.5210 gram air-dried salt gave 0.1797 gram $BaSO_4$.
III. 1.1406 grams air-dried salt lost at 120° 0.0314 gram H_2O.
IV. 1.6890 grams air-dried salt lost at 138° 0.0491 gram H_2O.

	Calculated for $Ba(C_4HClBrSO_4)_2.H_2O$	I.	II.	III.	IV.
			Found.		
Ba	20.27	20.35	20.28	...	...
H_2O	2.66	...	...	2.75	2.90

I. 0.7017 gram salt dried at 138° gave 0.2496 gram $BaSO_4$.
II. 0.9112 gram salt dried at 138° gave 0.3259 gram $BaSO_4$.
III. 0.7824 gram salt dried at 130° gave 0.2795 gram $BaSO_4$.

	Calculated for $Ba(C_4HClBrSO_4)_2$.	I.	II.	III.
			Found.	
Ba	20.82	20.92	21.03	21.00

[1] This Journal **10**, 414; and Proc. Am. Acad. **23**, 211.

The solubility of the salt in cold water was also determined in the usual way.

I. 20.5274 grams solution saturated at 18° gave 0.3105 gram $BaSO_4$.

II. 21.5098 grams solution saturated at 18° gave 0.3276 gram $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	III.
4.27	4.30

Calcic *aa-Chlorbromfurfuran-β-Sulphonate*, $Ca(C_4HClBrSO_4)_2.2H_2O$.

The calcium salt crystallises in large concentrically grouped needles which contain two molecules of water. It is permanent in the air or over sulphuric acid.

I. 0.6429 gram air-dried salt gave 0.1480 gram $CaSO_4$.

II. 0.7372 gram air-dried salt gave 0.1702 gram $CaSO_4$.

III. 0.7580 gram air-dried salt lost at 160° 0.0468 gram H_2O.

	Calculated for $Ca(C_4HClBrSO_4)_2.2H_2O$.	I.	Found. II.	III.
Ca	6.70	6.77	6.79	...
H_2O	6.03	...	...	6.17

I. 0.4463 gram salt dried at 160° gave 0.1097 gram $CaSO_4$.

II. 0.4230 gram salt dried at 165° gave 0.1045 gram $CaSO_4$.

	Calculated for $Ca(C_4HClBrSO_4)_2$.	I.	Found. II.
Ca	7.13	7.23	7.26

Plumbic *aa-Chlorbromfurfuran-β-Sulphonate*, $Pb(C_4HClBrSO_4)_2.H_2O$.

The lead salt is but sparingly soluble in cold water, and its solubility is but little increased by heat. By evaporation *in vacuo* over sulphuric acid it was obtained in compact hemispherical masses. The salt may be dried without decomposition at 100°, but at a somewhat higher temperature it begins to decompose, and at 140° it is completely charred.

I. 0.5743 gram air-dried salt gave 0.2339 gram $PbSO_4$.

II. 1.5077 grams air-dried salt lost at 100° 0.0410 gram H_2O.

	Calculated for Pb(C$_4$HClBrSO$_4$)$_2$.H$_2$O.	Found.	
		I.	II.
Pb	27.75	27.83	...
H$_2$O	2.41	...	2.72

0.7187 gram salt dried at 100° gave 0.3000 gram PbSO$_4$.

| | Calculated for Pb(C$_4$HClBrSO$_4$)$_2$. | Found. |
| Pb | 28.39 | 28.52 |

Potassic aa-Chlorbromfurfuran-β-Sulphonate, KC$_4$HClBrSO$_4$.

The potassium salt is very soluble in hot water, less soluble in cold water. The hot concentrated solution solidifies on cooling, with the separation of small shining anhydrous plates.

I. 0.5801 gram air-dried salt gave 0.1699 gram K$_2$SO$_4$.

II. 0.5479 gram air-dried salt gave 0.1625 gram K$_2$SO$_4$.

	Calculated for KC$_4$HClBrSO$_4$.	Found.	
		I.	II.
K	13.05	13.15	13.31

Action of Chlorine.

We attempted to prepare *aa*-dichlorfurfuran-β-sulphonic acid by the action of chlorine upon the salts of β-sulpho-δ-chlorpyromucic acid. We found, however, that the reaction in this case was not as simple as that with bromine, in that oxidation of the furfuran-sulphonic acid began long before one molecule of chlorine had been added, and that sulphofumaric acid and even sulphuric acid were formed before the whole of the original sulphochlorpyromucic acid had disappeared. While it was not difficult to isolate a salt which had substantially the properties and the composition of a baric dichlorfurfuran sulphonate, we were unable to prepare by any variation of the method, a product from which we could obtain perfectly satisfactory results.

Action of Nitric Acid.

We studied the action of nitric acid upon β-sulpho-δ-chlorpyromucic acid, only so far as to satisfy ourselves that no nitro-acid could be formed in this way, and that sulphofumaric acid was the chief product of the reaction.

LXXVII.—ON CERTAIN PRODUCTS OF THE DRY DISTILLATION OF WOOD: METHYLFURFUROL AND METHYLPYROMUCIC ACID.[1]

By Henry B. Hill and Walter L. Jennings.

Several years ago, one of us described[2] the occurrence of furfurol in not inconsiderable quantity among the products of the dry distillation of wood at low and carefully regulated temperatures, as carried on at Brooklyn under the direction of Dr. E. R. Squibb. Although attempts were made at the time to separate by fractional distillation the higher-boiling constituents of the crude furfurol, ordinary boiling-flasks alone were employed, and the results were so far from encouraging that a more thorough investigation was for the moment relinquished. The gradual accumulation of larger quantities of these higher-boiling oils encouraged us to renew the investigation, and we soon found that fractions of constant boiling-point could readily be isolated by using in the distillation the extremely effective bead-columns of Hempel.[3] The most noticeable fraction which we obtained was one boiling at 184°–186°. This proved to contain chiefly methylfurfurol, a preliminary account of which was published[4] soon after its identification. A few months later Maquenne,[5] and Bieler and Tollens,[6] quite independently of each other, found the same methylfurfurol among the products formed by the distillation of several species of seaweed with dilute sulphuric acid, and showed that the fucusol of Stenhouse[7] was a mixture of furfurol with this methylfurfurol. Shortly afterwards the same body was obtained by the action of dilute sulphuric acid upon isodulcite by Maquenne,[8] who pointed out that this mode of formation, taking into consideration the constitution of isodulcite as established by Fischer and Tafel,[9] proved the

[1] A part of the work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1892, by Walter L. Jennings, then candidate for the degree of Doctor of Philosophy. The paper was presented at a meeting of the American Academy of Arts and Sciences, held November, 1892.

[2] This Journal **3**, 34; and Proc. Am. Acad. **16**, 155.

[3] Ztschr. anal. Chem. **20**, 502.

[4] Ber. d. chem. Ges. **22**, 607.

[5] Comptes rendus **109**, 571.

[6] Ber. d. chem. Ges. **22**, 3062; Ann. Chem. (Liebig) **257**, 110.

[7] Ann. Chem. (Liebig) **74**, 278.

[8] Comptes rendus **109**, 603.

[9] Ber. d. chem. Ges. **20**, 1092; **21**, 2173.

methyl group to be in the δ-position. This conclusion of Maquenne concerning the structure of methylfurfurol was afterward confirmed in this laboratory by a study of the product formed by the action of aqueous bromine upon methylpyromucic acid, and a brief description of this reaction was published at the time.[1] Instead of the half-aldehyde of fumaric acid,

$$C_2H_2{<}{\begin{matrix}COOH\\COH\end{matrix}}$$
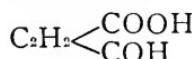
which is formed under like conditions from pyromucic acid, methylpyromucic acid yields the acetacrylic acid of Wolff,[2]

$$C_2H_2{<}{\begin{matrix}COOH\\COCH_3\end{matrix}}$$
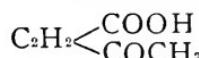
and the formation of this ketone acid proves that the methyl group is attached to the δ carbon atom of the furfuran ring. We have also studied the action of dry bromine upon methylpyromucic acid, and have found that a somewhat unstable tetrabromide may be prepared, although the substitution-products are more readily obtainable. For the preparation of the tetrabromide the temperature must be kept below 0°; if the bromine be allowed to act at ordinary temperatures, a brommethylpyromucic acid is formed which melts at 150°–151°, and contains the bromine in the furfuran ring, while at higher temperatures (50°–60°) the bromine enters chiefly the side-chain and forms ω-brommethylpyromucic acid melting at 147°–148°. The formation of these two isomeric products at different temperatures recalls the analogous reactions in the aromatic series, and the analogy is completely borne out by the behavior of the two acids. We have also made a dibrommethylpyromucic acid melting at 175°, in which one bromine atom is situated in the furfuran ring, the other in the side-chain. By the action of water upon the two acids which contain halogen in the side-chain we have made the corresponding oxy-acids.

We had intended to make a thorough study of the higher boiling fractions of the crude furfurol, and to determine as far as possible the nature of the various constituents; but the investigation of the methylfurfurol and its derivatives proved so much more attractive that we have contented ourselves with the partial examination of the fractions boiling at 200°–215° and established in them the presence of guaiacol.

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[1] Ber. d. chem. Ges. **23**, 452.   [2] *Ibid.* **20**, 426; Ann. Chem. (Liebig) **254**, 245.

METHYLFURFUROL.

The material which we had at our disposal was that portion of the crude furfurol which remained behind at 175° on distilling the oil several times from ordinary retorts or boiling flasks. It had been accumulating for more than ten years, was dark in color, somewhat thick and viscous, and left on distillation a large tarry residue. We therefore distilled it from small copper retorts until signs of decomposition appeared. While the earlier investigations had shown that the temperature could be pushed to over 300° without essential decomposition, we now found that carbonisation ensued at about 250°. At first we ascribed this difference in behavior to decomposition effected by long standing of the material; but we subsequently learned that changes had also been made in the meantime in the factory methods, and that it was quite possible that the greater part of our material had been subjected to the newer treatment. A special examination of the residue yielded by the distillation of nearly fifty kilograms of a fresh supply of crude furfurol showed that in this case decomposition also set in at 250°, so that no products boiling above this temperature could be obtained.

On fractioning with the aid of a Hempel column the yellow distillate which was first obtained, we soon found that it still contained considerable quantities of furfurol, and aside from this, that a comparatively large portion distilled between 180° and 185°, and a smaller portion at 200°–220°. As the distillation progressed, the intermediate fractions diminished in such a way that it became evident that but one body could be isolated between 165° and 200°, and that it boiled at a temperature not far from 185° (uncorrected). We therefore continued the distillation, taking two-degree fractions, and were able to collect a large portion which boiled with satisfactory constancy at 184°–186°. As the material thus obtained showed the character of an aldehyde, a portion of it was shaken with a concentrated solution of acid sodic sulphite. The oil was almost wholly dissolved with the evolution of heat, and as the solution cooled it solidified with the separation of flat radiating prisms. These were drained thoroughly upon the pump, washed with cold alcohol, pressed, and dried. The dry crystals were then decomposed by the requisite amount of sodic carbonate in aqueous solution, and the liberated aldehyde distilled over with

steam. The oil which passed over was then dried with fused calcic chloride and distilled. It showed the constant boiling-point 187°, with the mercury column completely in vapor and under a pressure of 766 mm. The boiling-point of a second preparation was found to be 186.5°–187° under a pressure of 760 mm. An analysis of the oil showed that its formula was $C_6H_6O_2$.

0.1995 gram substance gave 0.4788 gram CO_2 and 0.0998 gram H_2O.

	Calculated for $C_6H_6O_2$.	Found.
C	65.45	65.43
H	5.45	5.56

The formula of the substance, together with its strongly marked resemblance to furfurol, identified it as a methylfurfurol, and by oxidation with moist silver oxide it could readily be converted into the corresponding methylpyromucic acid.[1]

Freshly distilled methylfurfurol is a nearly colorless oil, with an odor closely resembling that of furfurol. On standing it grows dark-colored apparently more rapidly than furfurol, and acquires an acid reaction. The compound which it forms with acid sodic sulphite crystallises in flat concentrically grouped prisms, which are usually rectangularly truncated. The salt dissolves in from two to three parts of water at ordinary temperatures. In the preliminary paper already referred to,[2] the statement was made that methyl-furfurol gave the characteristic color reaction with a solution of rosaniline decolorised by sulphurous acid. We have found, however, that carefully purified methylfurfurol gives to this solution but a slight brown-red, or, if added in larger quantity, but a pale wine-red coloration, and are forced to conclude that the color formerly observed was due to a slight admixture of furfurol. It gives, however, with diazobenzol sulphonic acid when tested in the manner described by Penzoldt and Fischer[3] a color identical in shade with that given by furfurol. With hydrochloric acid and resorcin it gives an orange-red, with pyrogallol a carmine-red condensation-product. Aniline acetate paper gives at first no color, or at best turns but a light yellow, but on standing a deep orange color is developed. With phenylhydrazine a liquid hydrazone is formed, which we have not further examined. The specific gravity of methylfurfurol we have found to be somewhat higher than given by Maquenne.[4] A freshly prepared sample made with

[1] See page 165. [2] Ber. d. chem. Ges. **22**, 607.
[3] *Ibid.* **16**, 657. [4] Ann. chim. phys. [6] **22**, 84.

great care gave us at 18° referred to water at the same temperature the specific gravity 1.1087, or 1.1072 referred to water at 4°. As the sample was slightly colored it was distilled twice in a stream of hydrogen, but the specific gravity was altered but a few units in the fifth decimal place. The original fraction 186°–187° (cor.) from which this sample was made gave a specific gravity of 1.1059. Maquenne found the specific gravity of his fraction 185°–187° to be 1.107, and of the portion boiling at 187° to be 1.104. In water methylfurfurol is more sparingly soluble than furfurol, and requires about thirty times its weight of water at ordinary temperatures for complete solution.

Since it was difficult to form even an approximate estimate of the relative amounts of furfurol and of methylfurfurol contained in the crude oil from an examination of the residues from previous distillations which we had at our disposal, we submitted to fractional distillation about 50 kilograms of the crude oil. We used a copper retort of eight litres' capacity, which was fitted with a suitable column made out of large thin-walled brass pipe and filled with glass beads. After repeated distillations we obtained about two per cent. of the material taken in the fraction boiling from 182°–186° (uncorrected), and sixty per cent. in the fraction boiling from 160°–165°. Although the absolute amounts doubtless would have been somewhat increased by further separation of the small intermediate fractions, the relative amounts could have been little altered.

Methylfurfuramide, $C_{15}H_{15}N_2O_3$.—An aqueous solution of methylfurfurol, when mixed with ammonic hydrate, gives after the lapse of some time a crystalline precipitate of methylfurfuramide. This substance crystallises in slender radiating needles, dissolves readily in alcohol, ether, chloroform, benzol or carbonic disulphide, but is more sparingly soluble in ligroin. The substance recrystallised from ligroin was found to melt at 86°–87°, and contained the proper percentage of nitrogen.

0.3510 gram substance gave 27.8 cc. of moist nitrogen at 22° and under a pressure of 759 mm.

	Calculated for $C_{15}H_{15}N_2O_3$.	Found.
N	9.03	8.96

GUAIACOL.

The larger fractions of the oil boiling above methylfurfurol were those which were collected between 200° and 220°, but even after long-continued distillation no substances of constant boiling-point could be isolated. While the oil did not appear to contain an alde-hyde in sensible quantities, a large portion of it was soluble in aqueous alkalies, and we thought it advisable to take advantage of this fact in order to simplify our task. The fractions 200°–215° were therefore united, shaken with a solution of sodic hydrate, and the aqueous emulsion distilled with steam as long as oil passed over. The alkaline solution was then acidified and again distilled with steam. The neutral oil when dried with calcic chloride dis-tilled at 210°–220°, and we have not yet examined it further. The oil which was soluble in the alkaline solution boiled between 200° and 205°, and the thermometer remained for a long time constant at 202°. The physical properties of this oil and the emerald-green color which ferric chloride developed in its alcoholic solution left no doubt in our minds that it was guaiacol, and we thought that it could possibly be most conveniently identified with precision by converting it into the tribromguaiacol of Tiemann and Koppe.[1] On adding bromine to an alcoholic solution according to their directions, however, we obtained an unsatisfactory product. The melting-point, although somewhat higher than that given by Tie-mann and Koppe (102°), was not sharp, and was little improved by repeated recrystallisation. As the inherent disadvantages in adding bromine to an alcoholic solution were sufficiently obvious, we substituted glacial acetic acid for the alcohol, and at once obtained a definite product. From 5 grams of our oil we obtained 8.3 grams of a highly crystalline, nearly colorless bromine deriva-tive, which melted at 111°–112°, and a single recrystallisation suf-ficed to raise the melting-point to 115°–116°. Further recrystalli-sation from alcohol or benzol failed to raise this melting-point. While our product thus melted 14° higher than the tribromguaia-col of Tiemann and Koppe, it agreed in other respects with their description, and the following analyses show that it had the same composition :

I. 0.2316 gram substance gave 0.1974 gram CO_2 and 0.0345 gram H_2O.

[1] Ber. d. chem. Gesell. **14**, 2017.

II. 0.1603 gram substance gave 0 2497 gram AgBr.
III. 0.1705 gram substance gave 0.2653 gram AgBr.

	Calculated for $C_7H_5Br_3O_2$.	I.	Found. II.	III.
C	23.27	23.25	...	...
H	1.39	1.65	...	...
Br	66.48	...	66.30	66.24

Since we had failed to identify our substance as guaiacol through the melting-point of this bromine derivative, we proceeded to prepare from it pyrocatechin. For this purpose we used, instead of the more usual hydriodic acid, hydrochloric acid, as W. H. Perkin, Jr.[1] had recently shown the decomposition was in this case nearly perfect if the reaction took place in sealed tube at 170°–180°. On opening the tube, a gas escaped which burned with a green-bordered flame. The aqueous solution was extracted with ether, and the crystalline residue which was left upon evaporating the ether was distilled. The substance boiled at 240°–242°, and the solidified distillate melted at 103°–104°. When recrystallised from benzol it formed colorless lustrous scales, which appeared under the microscope to be rectangular plates, and melted sharply at 104°. The boiling-point of pyrocatechin is usually given at 240°–245°, and the melting-point was found by Fittig and Mager[2] to be 104°. In aqueous solution our product also gave with ferric chloride an emerald-green coloration which turned to a violet-red on the addition of sodic carbonate. It was thus established with precision that pyrocatechin had been formed by heating with hydrochloric acid the oil under investigation, and the latter was therefore in its turn identified as guaiacol. It seems to us probable that the tribromguaiacol which we have just described is identical with that of Tiemann and Koppe, and that the low melting-point which they observed was due to by-products introduced by their method of preparation. A more extended investigation of the matter was, however, wholly foreign to our line of work. We hope that the constituents of the crude furfurol which boil above 200° may be studied more fully in this laboratory at some future time.

METHYLPYROMUCIC ACID.

In order to prepare from methylfurfurol the corresponding methylpyromucic acid, we first attempted to follow the methods

[1] J. Chem. Soc. **57**, 589. [2] Ber. d. chem. Ges. **8**, 365.

which we had already used in the manufacture of pyromucic acid from furfurol. We found, however, that alkaline hydrates, either in alcoholic or aqueous solution,[1] gave us an extremely poor product in very unsatisfactory quantity. Although the experiments of Lessing in the laboratory of Limpricht[2] upon the oxidation of furfurol with argentic oxide gave us little hope that we could in this way conveniently prepare large quantities of methylpyromucic acid, no better method suggested itself to us at the time, and we were forced to adopt it. To our surprise, we found that we could easily obtain in this way a weight of methylpyromucic acid which nearly equaled that of the aldehyde taken, and that we could also obtain from furfurol under the same conditions an equally satisfactory yield of pyromucic acid. From methylfurfurol we obtained as a maximum 84 per cent. of the theoretical yield of methylpyromucic acid, from furfurol 82 per cent. of the calculated amount of acid. As the weight of acid remaining in solution after precipitation with hydrochloric acid was in neither case taken into account, the reaction may fairly be called quantitative. The large yield which we obtained was doubtless due in part to a slight modification of the ordinary method of procedure, which we shall presently describe. Still we had no difficulty in obtaining from 10 grams of furfurol in the usual way 8.5 grams of argentic pyromucate, and from the acidified mother-liquor by extraction with ether 2.9 grams of pyromucic acid, so that the total yield of pyromucic acid in this case was 7.25 grams, or 62.1 per cent. of the theoretical amount.

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[1] For many years a concentrated aqueous solution of sodic hydrate has been used at this laboratory in the preparation of pyromucic acid. Our method has been, however, essentially different from that recommended by H. Schiff (Ann. Chem. (Liebig) **239,** 374; **261,** 254), in that we have destroyed the furfuryl alcohol by hydrochloric acid instead of removing it with ether. The saving of time and of ether has more than compensated us for the somewhat diminished yield. 2 litres of furfurol are very gradually mixed with 1200 cc. of aqueous sodic hydrate (1:1), taking care by constant stirring and cooling that the thick paste does not grow hot. On the following day 2 litres of concentrated hydrochloric acid are gradually added, the temperature toward the end being allowed to rise somewhat to facilitate the complete decomposition of the furfuryl alcohol. If the temperature rises too rapidly the reaction becomes violent. The furfuryl alcohol is in any case converted into a tough leathery substance, which grows brittle on standing with the excess of hydrochloric acid. The slightly colored mother-liquor is drained off, the residue crushed in an iron mortar, 4 litres of water added, and then calcic hydrate, until the solution is permanently alkaline. After standing for several days, the solution being kept slightly alkaline, the pyromucic acid is carried completely into solution. The filtrate is but slightly colored, and this slight color may be almost wholly removed by bone-black. The yield of nearly colorless pyromucic acid which may be obtained in this way amounts to from 35 to 40 per cent. of the weight of furfurol taken.

[2] Ann. Chem. (Liebig) **165,** 279. Lessing obtained a weight of pyromucic acid equal to but 14 per cent. of the weight of furfurol employed, or but 12 per cent. of the theoretical amount.

All the methylpyromucic acid which we have used in our investigations we have made by the following method. 10 grams of methylfurfurol were added to about 50 grams of well-washed argentic oxide suspended in about 800 cc. of hot water, and the whole heated quickly to boiling. When the reaction appeared to be complete, pure sodic carbonate was added in quantity sufficient to precipitate the silver which had been carried into solution, and the feebly alkaline solution again boiled. When the fresh well-marked reduction which then ensued was finished, the solution was filtered, evaporated to small volume, again filtered, and acidified with hydrochloric acid. The acid which separated as the solution cooled was nearly colorless, and as a rule a single recrystallisation was sufficient to raise the melting-point to the proper point. The slight color could be most conveniently removed, if necessary, by treating a solution of the calcium salt with bone-black.

0.2067 gram of the acid gave 0.4321 gram CO_2 and 0.0900 gram H_2O.

	Calculated for $C_6H_6O_3$.	Found.
C	57.14	57.01
H	4.76	4.84

Methylpyromucic acid melts at 108°–109°, and sublimes readily at low temperatures. It is readily soluble in alcohol, ether, chloroform, or hot benzol, more sparingly soluble in cold benzol, and almost insoluble in carbonic disulphide. It is extremely soluble in hot water, and on cooling it separates from concentrated solutions in short, thick six-sided prisms, or in small six-sided plates formed by the development of these prisms parallel to the basal plane. From dilute solutions it frequently separates in feathery or bladed aggregations. The solubility of the acid in cold water we determined by titration with a standard solution of baric hydrate, using phenolphthalein as an indicator.

I. 22.293 grams of a solution saturated at 20° required for neutralisation 15.3 cc. of a solution of baric hydrate, containing 0.01864 gram BaO_2H_2 in 1 cc.

II. 19 665 grams of a solution saturated at 20° required for neutralisation 13.55 cc. of the above solution of baric hydrate.

According to these determinations an aqueous solution saturated at 20° contained the following percentages of acid:

I.	II.
1.89	1.89

Methylpyromucic acid is therefore decidedly less soluble in water at ordinary temperatures than pyromucic acid.[1]

For the further characterisation of the acid we have prepared a number of its salts.

Baric methylpyromucate, $Ba(C_6H_5O_3)_2$.—This salt we made by boiling an aqueous solution of the acid with baric carbonate. The salt is readily soluble in cold water, somewhat less soluble in hot water, and separates on evaporation in small colorless octahedral crystals which are anhydrous. The salt thoroughly dried by pressure suffered no material loss of weight on exposure to the air.

I. 0.3366 gram air-dried salt gave 0.2023 gram $BaSO_4$.

II. 0.4261 gram air-dried salt gave 0.2562 gram $BaSO_4$.

	Calculated for $Ba(C_6H_5O_3)_2$.	Found. I.	II.
Ba	35.40	35.34	35.34

The solubility of the salt in water at ordinary temperatures we determined in the usual way.

I. 5.8353 grams of a solution saturated at 19.6° gave 0.7950 gram $BaSO_4$.

II. 5.5326 grams of a solution saturated at 19.6° gave 0.7526 gram $BaSO_4$.

According to these determinations, the aqueous solution saturated at 19.6° contained the following percentages of the salt:

I.	II.
22.62	22.59

In order to determine the solubility at higher temperatures we followed essentially the method recommended by V. Meyer.[2]

I. 6.8590 grams of a solution saturated at 99° gave 0.8655 gram $BaSO_4$.

II. 5.1805 grams of a solution saturated at 99° gave 0.6480 gram $BaSO_4$.

The aqueous solution saturated at 99° therefore contained the following percentages of the salt:

---

[1] According to Houton Labillardière (Ann. chim. phys. [2], **9**, 368), pyromucic acid is soluble in 26 parts of water at 15°. This result is confirmed by approximate determinations made in this laboratory as a guide in the preparation of pyromucic acid. It was found that 100 cc. of a solution saturated at 17° contained 3.35 grams of the acid, and that 100 cc. of a saturated solution of sodic chloride at the same temperature dissolved 0.60 gram of the acid. The erroneous statement made in the preliminary description of the acid (Ber. d. chem. Gesell. **22**, 608), that it was "somewhat more readily soluble in water" than pyromucic acid, was based upon rough quantitative results obtained in recrystallising from water the small quantity of the acid which I then had at my disposal.—H. B. H.

[2] Ber. d. chem. Ges. **8**, 1002.

	I.		II.
	20.95		20.78

Calcic methylpyromucate, $Ca(C_6H_5O_3)_2.2H_2O$.—The calcium salt is readily soluble in cold water, and the solubility is slightly increased by heat. It crystallises in clusters of long radiating needles which contain two molecules of water.

I. 0.3544 gram air-dried salt gave 0.1475 gram $CaSO_4$.

II. 0.3184 gram air-dried salt gave 0.1333 gram $CaSO_4$.

III. 0.8481 gram air-dried salt lost at 110° 0.0931 gram H_2O.

IV. 0.5421 gram air-dried salt lost at 110° 0.0596 gram H_2O.

	Calculated for $Ca(C_6H_6O_3)_2.2H_2O$.	I.	II.	Found. III.	IV.
Ca	12.28	12.24	12.31	...	...
H_2O	11.04	...	...	10.97	10.99

I. 0.2688 gram salt dried at 110° gave 0.1254 gram $CaSO_4$.

II. 0.3109 gram salt dried at 110° gave 0.1452 gram $CaSO_4$.

	Calculated for $Ca(C_6H_5O_3)_2$.	I.	Found. II.
Ca	13.79	13.72	13.74

In determining the solubility of the salt, the calcium was precipitated as oxalate and weighed as sulphate.

I. 6.8529 grams of a solution saturated at 20.2° gave 0.4104 gram $CaSO_4$.

II. 7.8851 grams of a solution saturated at 20.2° gave 0.4688 gram $CaSO_4$.

The aqueous solution saturated at 20.2° therefore contained the following percentages of the anhydrous salt:

	I.		II.
	12.77		12.68

Argentic methylpyromucate, $AgC_6H_5O_3$.—This salt may readily be made by precipitation of a soluble salt with silver nitrate, and may be recrystallised from hot water. It is sparingly soluble even in boiling water, and crystallises from aqueous solution in fine slender needles.

I. 0.2110 gram salt gave on ignition 0.0977 gram Ag.

II. 0.4007 gram salt gave on ignition 0.1855 gram Ag.

	Calculated for $AgC_6H_5O_3$.	I.	Found. II.
Ag	46.34	46.30	46.29

Sodic methylpyromucate, $NaC_6H_5O_3$.—The sodium salt is exceedingly soluble even in cold water. It separated from its solution in dilute alcohol after long standing in compact clusters of small anhydrous needles.

I. 0.2752 gram air-dried salt gave 0.1325 gram Na_2SO_4.

II. 0.4240 gram air-dried salt gave 0.2043 gram Na_2SO_4.

	Calculated for $NaC_6H_5O_3$.	Found. I.	II.
Na	15.53	15.60	15.53

Potassic methylpyromucate, $KC_6H_5O_3$.—The potassium salt is also very readily soluble in cold water, and crystallises in spherical aggregations of short prisms which appear to be anhydrous.

0.3385 gram air-dried salt gave 0.1790 gram K_2SO_4.

	Calculated for $KC_6H_5O_3$.	Found.
K	23.83	23.74

Ethyl methylpyromucate, $C_6H_5O_3C_2H_5$.—The ethyl ether of the acid we made in the ordinary way, by saturating a solution in an equal weight of absolute alcohol with hydrochloric acid. The excess of hydrochloric acid was then driven off at a gentle heat, the ether precipitated with water, washed with a dilute solution of sodic carbonate, dried with calcic chloride and distilled. The whole product passed over between 212° and 215°, and by far the greater portion showed the constant boiling-point 213°–214° with the mercury column completely in vapor under a pressure of 766 mm. The ether showed no tendency toward crystallisation when cooled with ice and salt.

I. 0.2363 gram substance gave 0.5404 gram CO_2 and 0.1392 gram H_2O.

II. 0.1570 gram substance gave 0.3585 gram CO_2 and 0.0921 gram H_2O.

	Calculated for $C_6H_5O_3C_2H_5$.	Found. I.	II.
C	62.34	62.36	62.27
H	6.49	6.54	6.52

Methylpyromucamide, $C_6H_5O_2NH_2$.—Ethyl methylpyromucate is readily attacked by concentrated aqueous ammonia, and the reaction is completed in the cold after the lapse of two days. The clear solution then yields on evaporation the corresponding amide in long colorless prisms which melt at 131°. It is readily soluble in alcohol, dissolves freely in hot benzol or ligroin, sparingly in

the cold, and may best be recrystallised from hot water, in which it is readily soluble.

I. 0.2207 gram substance gave 22.8 cc. of moist nitrogen at 28° and under a pressure of 762 mm.

II. 0.1839 gram substance gave 19.1 cc. of moist nitrogen at 26° and under a pressure of 751 mm.

	Calculated for $C_6H_5O_2NH_2$.	Found.	
		I.	II.
N	11.20	11.36	11.38

Action of Bromine and Water.

Although Maquenne[1] had shown that the ready formation of methylfurfurol from isodulcite led directly to the conclusion that it must contain its methyl group in the δ position, it seemed desirable to establish this point by independent facts. Since pyromucic acid could readily be oxidised by bromine in aqueous solution, and converted into well marked bodies of the maleic acid group, it seemed probable that methylpyromucic acid would also yield analogous products. It was soon found that homogeneous products could not easily be obtained by using an excess of bromine, as is the case with pyromucic acid. Although a crystalline derivative could be obtained under certain conditions, the yield was not satisfactory, and viscous products were also formed. With two molecules of bromine, however, it was easy to reach definite results. Limpricht[2] showed in 1873 that pyromucic acid could be converted into a body which he called the half-aldehyde of fumaric acid, by the action of two molecules of bromine upon its aqueous solution, and v. Baeyer[3] subsequently proved that fumaric acid could be formed from this by the action of argentic oxide. It was evident, if methylpyromucic acid was decomposed in an analogous fashion, that there should be formed either an homologous aldehyde acid, or a ketone acid, according to the position of the methyl group in the furfuran ring. The formation of a ketone aldehyde under these conditions did not seem possible since Hill and Sanger[4] had shown that the aldehyde group in analogous reactions is invariably formed from the δ carbon of the pyromucic acid. The product formed from methylpyromucic acid under these conditions proved to be a ketone acid, and a brief description of the results of a preliminary examination which was undertaken at

[1] Comptes rendus **109**, 603.   [2] Ann. Chem. (Liebig) **165**, 285.
[3] Ber. d. chem. Ges. **10**, 1362.   [4] Proc. Am. Acad. **21**, 185.

the time by Mr. W. S. Hendrixson[1] and one of us was published elsewhere about two years ago. For the sake of completeness an account of these preliminary experiments will be included in the description of our own work, and we also owe to Mr. Hendrixson the analytical data which we publish. If methylpyromucic acid is suspended in about fifteen times its weight of cold water, and the vapor of bromine is slowly passed in by means of a current of air, the color of the bromine is quickly discharged, and the acid goes into solution with the escape of carbonic dioxide. When exactly two molecules of bromine have been added, the whole is allowed to stand for a short time, and the colorless solution then thoroughly extracted with ether. The ether left upon evaporation a crystalline body which was recrystallised from boiling benzol, and finally from water. An analysis showed that the formula of the substance was $C_5H_6O_3$.

0.2461 gram substance gave 0.4734 gram CO_2 and 0.1185 gram H_2O.

	Calculated for $C_5H_6O_3$.	Found.
C	52.64	52.47
H	5.26	5.35

The new body was readily soluble in hot water, more sparingly soluble in cold water, and was acid in its character. It dissolved readily in alcohol, ether, or boiling chloroform, more sparingly in cold chloroform. In hot benzol it was quite readily soluble, and very sparingly soluble in cold benzol, carbonic disulphide, or ligroin. It crystallised in long slender lustrous needles, which melted at 122°–123°. Recrystallisation from various solvents failed to raise the melting-point, but after several careful sublimations it melted at 123°–124°. The formula of this acid was further controlled by an analysis of its silver salt, which was prepared by the cautious addition of ammonic hydrate to a solution of the acid containing argentic nitrate. The salt can be recrystallised from boiling water without difficulty, and forms concentrically clustered six-sided plates.

I. 0.2237 gram salt gave 0.1901 gram AgBr.
II. 0.2926 gram salt gave 0.2484 gram AgBr.

	Calculated for $AgC_5H_5O_3$.	Found. I.	II.
Ag	48.87	48.81	48.76

[1] Ber. d. chem. Ges. **23**, 452.

The acid which had thus been formed from methylpyromucic acid corresponded well with the description of the acetacrylic acid which Wolff[1] had shortly before made through the decomposition of β-bromlaevulinic acid. Its melting-point, however, was given by Wolff as 125°–125.5°, although he adds in a more recent paper[2] that impurities otherwise imperceptible may depress the melting-point from two to three degrees. In order to compare the two acids, we have ourselves made the acetacrylic acid of Wolff from β-bromlaevulinic acid. In the preparation of the β-bromlaevulinic acid we followed with precision the directions of Wolff. The complete purification of the crude acid was in our hands attended with great loss of time and material, and, even after repeated recrystallisation from carbonic disulphide, we failed to raise the melting-point above 58°, while Wolff gives 59° as the melting-point of the pure acid. Under these circumstances we did not attempt to prepare pure β-bromlaevulinic acid in larger quantity, but decomposed with sodic acetate in an acetic acid solution a preparation which melted at 55°–56°. The acetacrylic acid which we thus obtained was to all appearance identical with that made from methylpyromucic acid. As was to be expected, its melting-point was somewhat low, 121°–123°, but after several recrystallisations from benzol melted at 123°–124°. Wolff[3] describes the silver salt of his acid as stellate needles, while the silver salt of our acid crystallised in well-formed six-sided plates. We convinced ourselves that the same six-sided plates were formed by the addition of argentic nitrate to a moderately concentrated solution of both acids, and that on recrystallisation these plates frequently formed dendritic aggregations. These dendritic forms only were seen if an insufficiently purified acid was used. While it is very possible that the acids which we had in our hands were in neither case absolutely pure, we cannot doubt the identity of the material from the two sources.

In order to identify still further our product with Wolff's acetacrylic acid, we dissolved it in chloroform and added at low temperature one molecule of bromine. The color of the bromine was discharged, and on evaporation a crystalline residue was obtained which melted after recrystallisation from a mixture of benzol and carbonic disulphide at 107°–108°. According to Wolff,[2] the $\alpha\beta$-dibromlaevulinic acid melts at this point. With phenylhydrazine

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[1] Ber. d. chem. Gesell. **20,** 426.   [2] Ann. Chem. (Liebig) **264,** 245.   [3] *Ibid.* p. 248.

our product also readily gave the corresponding hydrazone, identical in every respect with the body described by Bender[1] and shortly afterward by Decker.[2] It crystallised in small yellow prisms, which melted at $156°–157°$, and dissolved in concentrated sulphuric acid with a red color. Analysis showed that it had the formula $C_{11}H_{12}N_2O_2$.

I. 0.2240 gram substance gave 0.5299 gram CO_2 and 0.1190 gram H_2O.

II. 0.2173 gram substance gave 26.6 cc. of moist nitrogen at $23°$ and under a pressure of 752 mm.

	Calculated for $C_{11}H_{12}N_2O_2$.	Found. I.	II.
C	64.71	64.52	...
H	5.88	5.90	...
N	13.73	...	13.64

Bromine in aqueous solution, therefore, converts methylpyromucic acid into acetacrylic acid according to the equation

$$C_6H_6O_3 + 2Br_2 + 2H_2O = C_5H_6O_3 + CO_2 + 4HBr.$$
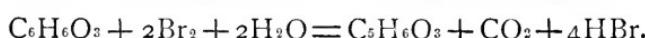
The formation of this ketone acid from methylpyromucic acid, while pyromucic acid under the same conditions yields an aldehyde acid, shows conclusively that the methyl group of the methylpyromucic acid stands in the δ place.

Action of Concentrated Sulphuric Acid.

We have thought that it might be possible to bring additional evidence as to the structure of the methylpyromucic acid through an investigation of the sulphonic acid derived from it. A study of the sulphonic acids derived from pyromucic acid had already shown that δ-sulphonic acids were always formed by the action of fuming sulphuric acid whenever the δ-hydrogen had not already been otherwise replaced; when the δ-hydrogen had been thus replaced, β-sulphonic acids were formed. Moreover, it was very easy to distinguish between the two isomers, in that bromine in aqueous solution instantly formed sulphuric acid from the δ-sulphonic acids, while the β-sulphonic acids were oxidised to products which retained the sulpho group. Methylpyromucic acid was added with careful cooling to three times its weight of fuming sulphuric acid, the whole allowed to stand for twenty-four hours,

[1] Ber. d. chem. Gesell. **21**, 2494.   [2] *Ibid.* **21**, 2937.

and the diluted solution then neutralised with baric carbonate as usual. The barium salt which was obtained by evaporating the filtered solution crystallised in long needles, which were frequently collected in globular aggregations. The salt was hardly more soluble in hot than in cold water, and could best be obtained by the evaporation of its cold aqueous solution *in vacuo* over sulphuric acid. In this respect it closely resembled the baric β-sulphopyromucate. An analysis showed that the salt was baric sulphomethylpyromucate, and that it contained five molecules of water of crystallisation.

I. 0.4798 gram air-dried salt gave 0.2597 gram $BaSO_4$.
II. 0.6678 gram air-dried salt lost at 165° 0.1383 gram H_2O.

	Calculated for $BaC_6H_4SO_6\,5H_2O$.	I.	Found. II.
Ba	31.78	31.83	...
H_2O	20.87	...	20.71

0.5272 gram salt dried at 165° gave 0.3598 gram $BaSO_4$.

	Calculated for $BaC_6H_4SO_6$.	Found.
Ba	40.17	40.13

Bromine water gave in an aqueous solution of the salt no precipitate even on boiling, but after this treatment with bromine, if baric hydrate was added to alkaline reaction, a white flocculent precipitate, which closely resembled baric sulphofumarate, appeared. This behavior showed conclusively that the sulpho group had not entered the furfuran ring in the δ-position, and the conclusion seems warranted that it had not done so only because the methyl group already occupied that place.

BROMMETHYLPYROMUCIC ACIDS.

Bromine acts readily upon methylpyromucic acid at ordinary temperatures, and substitution is so easily effected that the isolation of an addition-product is a matter of considerable difficulty. The instability of the addition-product renders it unsuitable for the preparation of substituted acids, and facilitates the formation of satisfactory products by direct substitution. The nature of the products thus formed is, however, largely dependent upon the temperature at which the reaction takes place. At low temperatures the bromine enters first the furfuran ring and afterwards the methyl group, while at higher temperatures the methyl group is

first attacked, although substitution apparently takes place at the same time to a certain extent in the ring. The facts which we have observed evidently correspond precisely with those so thoroughly established in the aromatic series. Moreover, those bodies which contain the halogen in the side-chain are extremely susceptible to double decomposition, and are even decomposed by heating for a short time with water. The halogen in the main ring, on the other hand, is held quite as persistently as that in the corresponding derivatives of pyromucic acid. The study of these bodies presented at first many difficulties, the solution of which cost us so much time and labor that we have been unable to carry our researches as far as we had hoped. Since one of us must now relinquish the work, we shall present the results we have obtained, although they are in many respects incomplete. Further researches upon the subject will be made in this laboratory. We are especially sorry that we have been unable to determine with precision the place in which the bromine enters the furfuran ring; while we have obtained by oxidation of the brommethylpyromucic acid in question an acid which is doubtless a bromacetacrylic acid, we have not yet been able to establish its structure and thus make it available in determining the constitution of the brommethylpyromucic acid from which it is formed. There can be but little doubt, however, that the bromine in this case enters the β-position, as it does with pyromucic acid itself as soon as the δ-hydrogen atom is replaced by bromine.

β(?)-Brommethylpyromucic Acid.

When dry bromine acts at ordinary temperatures upon methylpyromucic acid, hydrobromic acid is at once evolved, and brommethylpyromucic acid is formed. The reaction is most readily controlled by the use of a solvent, and we have found glacial acetic acid most convenient for the purpose. We have found it necessary to add decidedly more than one molecule of bromine, and the best results were obtained by using three atoms. The methylpyromucic acid is dissolved in one and a half times its weight of glacial acetic acid (99.5 per cent.), and the necessary amount of bromine carefully added, taking care that the temperature does not rise above 17°. After standing for some time at ordinary temperatures, the greater part of the hydrobromic acid

is expelled *in vacuo* over lime, the residue poured into water, and the acid extracted with ether. The crude acid left on the distillation of the ether we have found it most advantageous to convert into the sodium salt with alcoholic sodic hydrate. The sodium salt is easily collected upon a filter, and the acid is then reprecipitated from its aqueous solution after decolorisation with bone-black. The acid may be further purified by several repetitions of the same process.

I. 0.2279 gram substance gave 0.2935 gram CO_2 and 0.0526 gram H_2O.

II. 0.1147 gram substance gave 0.1055 gram AgBr.

	Calculated for $C_6H_5BrO_2$.	Found. I.	II.
C	35.12	35.13	...
H	2.44	2.56	...
Br	39.02	...	39.15

Brommethylpyromucic acid crystallises in colorless branching needles, which melt at 150°–151°. It is readily soluble in alcohol, ether, or chloroform, somewhat sparingly soluble in cold, more readily in hot benzol. In carbonic disulphide or ligroin it dissolves but sparingly even on boiling. It is somewhat sparingly soluble in hot water, and is deposited in clusters of branching needles as the solution cools. The solubility of the acid in water at ordinary temperatures we determined in the usual way. We neutralised with baric carbonate the solution of the acid, and determined as sulphate the barium which had been dissolved.

I. 17.598 grams of a solution saturated at 21.4° gave 0.0271 gram $BaSO_4$.

II. 16.031 grams of a solution saturated at 21.4° gave 0.0264 gram $BaSO_4$.

The aqueous solution saturated at 21.4° therefore contained the following percentages of the acid :

I.	II.
0.27	0.29

For the further characterisation of the acid we also prepared certain of its salts.

Baric brommethylpyromucate, $Ba(C_6H_4BrO_3)_2.4H_2O$. — This salt may readily be made from a solution of the ammonium salt by precipitation. It is sparingly soluble in cold water, more readily soluble in hot water, and crystallises from the hot aqueous solution

on cooling in dendritic needles, which contain four molecules of water. The salt is permanent in the air, but effloresces rapidly over sulphuric acid.

I. 0.4478 gram air-dried salt gave 0.1690 gram $BaSO_4$.

II. 0.8747 gram air-dried salt lost at 110° 0.1030 gram H_2O.

	Calculated for $Ba(C_6H_4BrO_3)_2 \cdot 4H_2O$.	Found.	
		I.	II.
Ba	22.20	22.19	...
H_2O	11.67	...	11.78

0.3664 gram salt dried at 110° gave 0.1558 gram $BaSO_4$.

	Calculated for $Ba(C_6H_4BrO_3)_2$.	Found.
Ba	25.14	25.00

The solubility of the salt in cold water was determined in the usual way.

I. 19.211 grams of a solution saturated at 20.2° gave 0.0518 gram $BaSO_4$.

II. 19.984 grams of a solution saturated at 20.2° gave 0.0466 gram $BaSO_4$.

The aqueous solution saturated at 20.2° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.63	0.55

Calcic brommethylpyromucate, $Ca(C_6H_4BrO_3)_2 \cdot 3H_2O$.—The calcium salt we prepared by precipitating with calcic chloride an ammoniacal solution of the acid. It crystallised from hot water in clusters of short needles which contained three molecules of water. The salt was permanent in the air, and lost but little in weight over sulphuric acid.

I. 0.2508 gram air-dried salt gave 0.0680 gram $CaSO_4$.

II. 0.5443 gram air-dried salt lost at 110° 0.0584 gram H_2O.

	Calculated for $Ca(C_6H_4BrO_3)_2 \cdot 3H_2O$.	Found.	
		I.	II.
Ca	7.97	7.98	...
H_2O	10.76	...	10.73

0.2724 gram salt dried at 110° gave 0.0584 gram $CaSO_4$.

	Calculated for $Ca(C_6H_4BrO_3)_2$.	Found.
Ca	8.93	8.86

In determining the solubility of the salt the calcium was precipitated as oxalate, and converted into sulphate before weighing.

I. 15.373 grams of a solution saturated at 20° gave 0.0189 gram CaSO₄.

II. 13.879 grams of a solution saturated at 20° gave 0.0170 gram CaSO₄.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.41	0.40

Argentic brommethylpyromucate, $AgC_6H_4BrO_3$.—The silver salt crystallises from hot water is spherical aggregations of dendritic needles.

0.0956 gram salt gave 0.0574 gram AgBr.

	Calculated for $AgC_6H_4BrO_3$.	Found.
Ag	34.61	34.48

Potassic brommethylpyromucate, $KC_6H_4BrO_3$.—This salt is very readily soluble even in cold water, and crystallises on slow evaporation of its aqueous solution in small anhydrous needles.

0.2789 gram salt gave 0.0993 gram K_2SO_4.

	Calculated for $KC_6H_4BrO_3$.	Found.
K	16.08	15.99

Action of Bromine and Water.

The whole behavior of the brommethylpyromucic acid showed conclusively that its bromine atom was situated in the furfuran ring. Although the bromacetacrylic acids had not yet been made, one of which would doubtless be formed by the oxidation of this brommethylpyromucic acid, and we therefore could not hope to determine whether the bromine was in the β or in the γ position, we nevertheless thought it best to investigate the products of oxidation. Brommethylpyromucic acid was suspended in thirty times its weight of water, and somewhat more than two molecules of bromine then slowly passed in by means of a current of air. The acid was readily carried into solution, and at the same time a small amount of an insoluble substance was formed. The filtered solution was extracted with ether, and the ethereal extract dried with calcic chloride. The viscous residue which was left on the distillation of the ether gradually solidified on standing over sulphuric acid *in vacuo.* This body proved to be an acid, containing bromine, readily soluble in water, but crystallising from benzol by evapora-

tion in rosettes. The melting-point of the recrystallised acid was found to be 61°. An analysis showed that the percentage of bromine contained in this acid agreed with that required by a bromacetacrylic acid.

0.1630 gram substance gave 0.1594 gram AgBr.

	Calculated for $C_6H_5BrO_3$.	Found.
Br	41.45	41.62

The oxidation had therefore taken precisely the same direction as that followed by the analogous decomposition of methylpyromucic acid, and through this product of oxidation it will doubtless be possible at some future time to fix the constitution of the brommethylpyromucic acid. A product apparently identical with this we have also obtained by the action of dilute nitric acid.

The insoluble product formed at the same time with the bromacetacrylic acid we unfortunately have not been able to study further. It is not acid in its character, contains a large amount of bromine, and crystallises from benzol in long colorless prisms, which melt at 90°–91°.

ω-Brommethylpyromucic Acid.

Although bromine in acting upon methylpyromucic acid at ordinary temperatures enters at once the furfuran ring, at the temperature of boiling carbonic disulphide or chloroform it attacks chiefly the methyl group, and a bromine derivative is formed in considerable quantity which differs wholly in its properties from the acid just described. The reaction is not perfectly simple, for we have found that we could obtain the best yield of the new product by using twice the theoretical quantity of bromine. We have dissolved the methylpyromucic acid in six times its weight of chloroform and slowly added to the boiling solution two molecules of bromine diluted with its own weight of chloroform. The evolution of hydrobromic acid at once begins, and frequently before the bromine is all added a heavy crystalline body separates from the hot solution. When the reaction is over, the chloroform is well cooled, the crystalline product, which amounts to about sixty per cent. of the weight of methylpyromucic acid taken, filtered off, and washed with cold chloroform. It may then be recrystallised from boiling chloroform or benzol.

I. 0.2152 gram substance gave 0.2758 gram CO_2 and 0.0490 gram H_2O.

II. 0.1176 gram substance gave 0.1079 gram AgBr.

	Calculated for $C_6H_5BrO_3$.	Found. I.	II.
C	35.12	34.95	...
H	2.44	2.53	...
Br	39.02	...	39.04

The ω-brommethylpyromucic acid crystallises in small clustered oblique plates which melt at 147°–148°. It is readily soluble in alcohol, ether, glacial acetic acid, or acetone, somewhat sparingly soluble in boiling benzol or chloroform, from which solvents it crystallises well on cooling. In boiling toluol it is freely soluble, sparingly soluble in the cold, and almost insoluble in carbonic disulphide. It is but slowly acted on by cold water, but on warming it is readily dissolved with decomposition. The solution contains hydrobromic acid in abundance, and upon evaporation a crystalline acid is obtained, which is free from bromine. This behavior, which is in such striking contrast with the extreme stability of the derivatives of pyromucic acid that contain halogen, sufficiently establishes the position of the bromine in the side-chain. It also effectually prevented the preparation of its salts by the ordinary methods.

Decomposition by Water.

The product formed by the action of water upon ω-brommethyl-pyromucic acid we have studied a little more in detail. After heating an aqueous solution for some time at 100° it was evaporated over lime *in vacuo*. The hard black crystalline residue was dissolved in hot water, filtered from the separated carbon, and again evaporated. The brownish vitreous crystalline mass thus obtained melted with decomposition at 158°–162°, and by recrystallisation from a mixture of toluol and absolute alcohol the melting-point could be raised to 162°–163°, although the body still melted with decomposition. A combustion showed that the substance was ω-oxymethylpyromucic acid.

0.2623 gram substance gave 0.4870 gram CO_2 and 0.1052 gram H_2O.

	Calculated for $C_6H_6O_4$.	Found.
C	50 70	50.63
H	4.23	4.46

ω-Oxymethylpyromucic acid is readily soluble in water, alcohol, or glacial acetic acid. In ether it is but slightly soluble, and in benzol, toluol, chloroform, or carbonic disulphide it is almost wholly insoluble. The barium salt of the acid is readily soluble in water, and is left as a varnish as its aqueous solution evaporates. From concentrated solutions it is thrown down as a flocculent precipitate on the addition of alcohol. We have not yet examined it further, and we have as yet found no other salts of a more inviting character.

The ease with which the ω-brommethylpyromucic acid entered into reaction with water naturally suggested the study of its behavior with other reagents. Unfortunately, we are unable to pursue our investigations in this direction, but further researches will be made in this laboratory.

In the preparation of the ω-brommethylpyromucic acid small quantities of the isomeric acid were also apparently formed. From the chloroform mother-liquors we obtained, after treatment with water and baric carbonate, a small amount of a crystalline acid which melted at 149°–151°, and in other respects resembled the brommethylpyromucic acid first described.

ωβ(?)-Dibrommethylpyromucic Acid.

If the brommethylpyromucic acid melting at 150°–151° is treated with bromine in boiling chloroform, a second atom of bromine enters the side-chain and a dibrommethylpyromucic acid is formed. The acid which separates on cooling or after partial evaporation of the solvent is washed with cold chloroform, and recrystallised from boiling toluol. This acid may perhaps more economically be made by the direct action of bromine at ordinary temperatures. Methylpyromucic acid is exposed over night to the vapor of three times its weight of bromine. The semi-liquid product is well washed with carbonic disulphide, next with chloroform, and the crystalline residue recrystallised from boiling toluol. Our analyses are not altogether satisfactory, but they leave no doubt as to the nature of the body.

I. 0.2877 gram substance gave 0.2735 gram CO_2 and 0.0418 gram H_2O.

II. 0.2086 gram substance gave 0.2748 gram AgBr.

	Calculated for $C_6H_4Br_2O_3$.	Found.	
		I.	II.
C	25.35	25.92	...
H	1.41	1.61	...
Br	56.33	...	56.07

This dibrommethylpyromucic acid crystallises in small oblique tabular crystals, which melt at 175° with decomposition. It is readily soluble in alcohol, ether, or glacial acetic acid, is but sparingly soluble in boiling benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. In boiling toluol it is quite readily soluble.

Action of Water.

On warming with water the acid is decomposed, hydrobromic acid is formed, and the solution then contains an oxybrommethylpyromucic acid. We prepared this acid first by treating with water the product formed by the vapors of bromine upon methylpyromucic acid, and separating it from the brommethylpyromucic acid melting at 151° which accompanied it by washing the mixed acids with benzol. The acid thus prepared from the crude material was absolutely identical with that afterwards made from the pure dibrommethylpyromucic acid. For analysis the substance was crystallised from a mixture of benzol and alcohol.

I. 0.1950 gram substance gave 0.2333 gram CO_2 and 0.0420 gram H_2O.

II. 0.1695 gram substance gave 0.1445 gram AgBr.

	Calculated for $C_6H_5BrO_4$.	Found.	
		I.	II.
C	32.58	32.63	...
H	2.26	2.39	...
Br	36.20	...	36.28

The ω-oxy-β(?)-brommethylpyromucic acid is readily soluble in alcohol and ether, very sparingly soluble in boiling carbonic disulphide, somewhat more readily soluble in boiling chloroform, from which it separates on cooling in obliquely terminated prisms. It is sparingly soluble in hot benzol, and almost insoluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and separates from dilute aqueous solutions in large obliquely terminated prisms, which contain one molecule of water. The crystals effloresce slowly over sulphuric acid, or even in the air after months of exposure, but we were unable to dehydrate them by heat without bringing about slight decomposition.

I. 0.4413 gram of acid crystallised from water lost over sulphuric acid 0.0328 gram H_2O.

II. 0.2117 gram of acid dried in desiccator over night gave 0.1681 gram AgBr.

	Calculated for $C_6H_5BrO_4.H_2O$.	Found. I.	Found. II.
H_2O	7.53	7.43	...
Br	33.47	...	33.80

The anhydrous acid melts at 153°–154°, and on cooling forms a viscous gummy mass. Sodium amalgam reduces the acid without difficulty, and yields the ω-oxymethylpyromucic acid already described. The barium salt of the acid is readily soluble in water, and crystallises in clustered short needles, but we have made no further study of its salts.

METHYLPYROMUCIC TETRABROMIDE.

We have already spoken of the instability of the addition product which methylpyromucic acid forms with bromine. We succeeded in isolating it by adding two molecules of bromine diluted with a little chloroform to a solution of methylpyromucic acid in five times its weight of chloroform well cooled with ice and salt. The bromine was slowly added with constant shaking, and at this low temperature but little hydrobromic acid was noticed. The addition-product soon began to separate in flat colorless needles, which were frequently twinned at right angles. After the bromine had all been added, the whole was allowed to stand for a short time, and the product then quickly filtered upon the pump and washed with cold chloroform. It was then pressed with filter-paper and dried in desiccator. As we found it impossible to recrystallise the substance without serious decomposition, we analysed it without further purification. On exposure to moist air it rapidly liquefied, and even over sulphuric acid it soon evolved hydrobromic acid in abundance. Analyses IV and V made with material which had stood for two and four days respectively in desiccator, show how rapidly the decomposition progresses.

I. 0.2695 gram substance gave 0.1668 gram CO_2 and 0.0383 gram H_2O.

II. 0.3509 gram substance gave 0.2182 gram CO_2 and 0.0467 gram H_2O.

III. 0.2011 gram substance freshly made gave 0.3393 gram AgBr.

IV. 0.1564 gram of same substance after two days gave 0.2601 gram AgBr.

V. 0.1520 gram of same substance after four days gave 0.2513 gram AgBr.

	Calculated for $C_6H_6Br_4O_3$.	I.	II.	Found. III.	IV.	V.
C	16.14	16.88	16.96	...	...	...
H	1.35	1.58	1.48	...	...	...
Br	71.74	...	...	71.81	70.79	70.37

Methylpyromucic tetrabromide is very sparingly soluble in carbonic disulphide or ligroin, somewhat less sparingly soluble in chloroform or benzol. In hot chloroform or benzol it dissolves more freely, but decomposition evidently ensues, for little unaltered substance crystallises on cooling. The substance melts at about 95° with decomposition, but the melting-point varies with the rapidity with which it is heated. Although the addition-product is so unstable, we have been able to find but few definite products resulting from its decomposition. Alcoholic sodic hydrate apparently destroys it completely. Sodic acetate in glacial acetic acid gives the brommethylpyromucic acid melting at 150°–151°, and the same acid also appears to be formed in the spontaneous decomposition of the body when exposed to the air.

Further investigation in this direction will be made in this laboratory.

XXII.—MOVEMENT OF THE ELEMENT PHOSPHORUS IN THE MINERAL, VEGETABLE, AND ANIMAL KINGDOMS, AND THE BIOLOGICAL FUNCTION OF THE LECITHINES.

By W. Maxwell.

In a preceding article[1] treating of the " Role of the Lecithines in Normal Germination," an endeavor was made to show the mode of movement of the element phosphorus, and the function of the

[1] This Journal **13**, 16.

lecithine bodies, during the period of germination and incipient growth of vegetable organisms.

Given varieties of seeds were selected, and in each of these the proportions of phosphorus present as mineral, in the form of phosphates, and likewise as organic phosphorus, in the form of lecithines, were determined. In the next place, further quantities of the same seeds were germinated, and the relative proportions of mineral and organic phosphorus in the germinated product redetermined. Three terms were observed in the period of germination, the last indicating the stage in the initial growth when the plantlet had consumed the whole of the reserve-material of the mother-seed, and was prepared to attach itself to extraneous matters for support.

The examinations of the products of germination of the several terms showed that the phosphorus which was contained in the original, or mother-, seed as a mineral phosphate had gradually decreased, and finally disappeared; and further, that in the proportion in which the decrease had occurred in the phosphorus present as phosphate, an increase had taken place in the amount of organic phosphorus observed in the form of lecithine.

It was thus shown that the organism of the seed possesses the property of eliminating the phosphorus from the mineral combination as a phosphate, and of causing it by a reorganisation to occur as a member of an organic molecule. It was likewise shown that the lecithine bodies are not only a medium by which the element phosphorus passes over from the mineral to the vegetable kingdom, but that the phosphorus taken up by the plant as a phosphate in aqueous solution is very probably in the first place converted into the form of an organic compound, and afterwards incorporated and utilised by the organism.

Having followed the movement of the element phosphorus from the mineral into the vegetable kingdom, it became of great moment and interest to investigate its mode of passage from the vegetable to the animal kingdom, and also to note any continued function of the lecithine bodies as a medium of transmission.

An investigation of the direct mode of passage of the element from the vegetable to the animal, upon the lines followed in the observation of its movement from the mineral to the vegetable, presented difficulties of a severe character; and in particular, the impossibility of controlling the conditions, and establishing terms

of development, such as were noted in the first part of the work. In view of these difficulties it was decided to select an animal organism in which the element phosphorus was contained in the mineral form as a phosphate, and likewise as a lecithine, corresponding to the mode of appearance of the element in the seed organism, and to pursue the movements and behavior of the element in processes and conditions analogous to those obtaining in vegetable germination.

The hen's egg was selected as the organism and material of the second part of the investigation. Not only does the egg contain phosphorus in inorganic combinations, but very notable quantities of lecithines are present as a significant constituent of the yolk. Moreover, the nature of the egg, and the inclosure of the processes and products of incubation very chiefly within the walls of the shell, fully provide for the control of conditions essential to the work.

The plan of the investigations conducted with the egg was in close resemblance to that adopted in the vegetable part of the work. In the first place, the relative proportions of phosphorus contained in the normal egg as mineral phosphate and lecithine respectively, were determined. Secondly, the eggs were incubated, the process of incubation being checked at specific terms of development of the embryo, and the relative amounts of mineral and organic phosphorus determined in the products of incubation. By such a plan of procedure the proportion, and the mode of combination of the phosphorus in the natural egg were, in the first place, ascertained. Also the relative proportions contained in mineral and organic forms at each stage of the period of incubation, and the movements of the element were observed during the time of progression of the embryo from the initial term to the time of leaving the shell.

The incubation was accomplished in the incubators in operation in the laboratory of the Bureau of Animal Industry, and under the direction of Dr. Theobald Smith, to whose courtesy the author was materially indebted.

The eggs were weighed before and after incubation, and the loss of substance which had occurred by the processes incident to the initial life of the embryo was determined. The weights of a given number of eggs before, after partial, and at the end of mature, incubation, are given in the following table :

Series I.

Egg.	Before Incubation.	After 15 days Incubation.	Loss of Weight.
No. 1.	58.66 grams.	49.74 grams.	15.21 per cent.
No. 2.	54.67	46.95	14.15
No. 3.	66.19	56.10	15.25

Mean = 14.90

Series II.

Egg.	Before Incubation.	After Mature Incubation.	Loss of Weight.
No. 1.	57.72 grams.	48.40 grams.	17.58 per cent.
No. 2.	50.42	40.85	19.00
No. 3.	51.79	42.20	18.71

Mean = 18.43

The ratio of loss of weight of the egg (including the shell[1]) during the process of incubation bears a close resemblance to the loss of substance occurring in vegetable germination; the loss in the latter being somewhat greater than in the former.

Preliminary work was done, with the eggs which had been incubated for the purpose of determining the loss of weight, in order to test the method of extraction and analysis, which method may be briefly given as follows:

In the treatment of the natural egg, the whole contents of the shell, including the white and yolk, were brought into an Erlenmeyer flask and boiled for 6 hours with absolute alcohol under a condenser. The alcoholic extract was distilled off and the residue extracted for 10 hours with ether. The egg material, which had been already boiled with alcohol, was reduced to a state of the greatest possible fineness in a mortar, and re-extracted for 10 hours with ether. The alcohol and ether extracts, containing the whole of the lecithine bodies present in the egg, were brought together and evaporated to a residue. The fatty residue was mixed with alkali salts and ignited, by which means the phos-

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[1] A decrease in the substance of the shell had very evidently occurred, and in one particular place. At a period of advanced development, it was observed that the membrane enveloping the embryo was attached to the inner surface of the shell, and at the place of attachment the shell had become noticeably thin, indicating that a decomposition of the lime carbonate had been effected by the action of the animal ferments, or the carbon dioxide disengaged in the processes of incubation. The latter gas, both from the shell and the organic tissues, would escape through the pores of the shell; the calcium, however, could not escape, and it is reasonable to suppose that it was utilised at a later period by the organism in the formation of bone.

phorus, present in the organic form as a lecithine, was converted into phosphates of sodium and potassium. The phosphorus, converted thus from an organic into an inorganic compound, was estimated in the usual way as magnesium pyrophosphate, and the lecithine-content calculated from the amount of pyrophosphate by means of the Hoppe-Seyler[1] factor.

The terms at which the incubation was stopped were as follows:

1. After 12 days incubation.
2. After 17 days incubation.
3. After 20 days incubation.

The temperature of the incubation during the period of incubation was 38°–40° C.

In the first place, a table showing the proportion of phosphorus present in the normal egg, as phosphate and lecithine respectively, will be considered.

Normal Egg.

| Egg. | Weight of Egg. | Pyrophosphate whose source was | | Lecithines in Egg. |
		Mineral.	Organic.	
No. 1.	65 grams.	0.1240 gram.	0.1852 gram.	2.07 per cent.
No. 2.	58	0.1018	0.1375	1.89
No. 3.	66	0.1307	0.1804	1.99

Mean = 1.98

The organism of the egg contains a very notable quantity of lecithine, the mean of the given examples being 1.98 per cent. of the weight of the egg.

I.— *Term of Incubation.*

| Egg. | Weight of Egg. | Pyrophosphates whose source was | | Lecithines in Egg. |
		Mineral.	Organic.	
No. 1.	56 grams.	0.1644 gram.	0.0855 gram.	1.11 per cent.
No. 2.	58	0.1623	0.1090	1.43
No. 3.	54	0.1435	0.0848	1.14

Mean of the three examples = 1.22

At the close of the first term, when the incubation had proceeded 12 days, a decrease of 38.7 per cent. is observed in the lecithine-content of the egg. It is also seen that in proportion as the amount of lecithine decreased, the mineral phosphorus, or phos-

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[1] Handbuch der physiol. und pathol. chem. Analyse, S. 169.

phate, increased. The uniform behavior of the eggs, which is
shown by the almost equal loss of each in the lecithine-content,
may be ascribed to their freshness, and that they were the product
of only two hens ; the smaller eggs being produced by the one
and larger eggs by the other.

II.— *Term of Incubation.*

Egg.	Weight of Egg.	Pyrophosphate whose source was		Lecithines in Egg.
		Mineral.	Organic.	
No. 1.	56 grams.	0.1447 gram.	0.1003 gram.	1.30 per cent.
No. 2.	58	0.1395	0.1140	1.45

Mean of the two examples = 1.38

The table indicates that during the longer period of incubation
a less decrease in the content of lecithines had taken place. In
the first examples, when the period of incubation had been 12
days, 38.7 per cent. of these bodies had disappeared. At the end
of 17 days incubation the eggs were found to contain 70.0 per cent.
of the original content of lecithines, the actual loss being only 30.1
per cent.

The results obtained in the study of incubation-products of the
period of 17 days were not in the direction anticipated. It is
apparent that the process of converting the phosphorus of the
lecithine bodies into phosphates had ceased in the organism, and
that a portion of the phosphates, already formed at the expense of
the organic phosphorus, had reverted to the lecithine form ;
otherwise the organism had increased the content of lecithines by
the use of the original phosphates present in the normal egg, con-
verting the phosphorus of those phosphates, in the first place, into
organic phosphorus bodies, or lecithines, in order to be used by
the organism in the same mode and for the same purpose as the
original lecithines. The latter is distinctly the more probable.

The results which were obtained with the products from the 17
days period of incubation are in close agreement, however, with
the observations made by Professor Hoppe-Seyler and his pupils.
He conducted his studies with the yolk of the egg, in which the
lecithines are located, and determined the lecithines, or organic
phosphorus, only, taking no cognisance of the mineral phosphorus
present in the normal egg. The results obtained by Hoppe-
Seyler[1] are given as follows :

[1] Handbuch der physiol. Chemie, S. 782 (Berlin, 1877).

Lecithines contained in yolk of natural egg, 10.720 per cent.
Lecithines after 10 days incubation,   8.406 per cent.
Lecithines after 17 days incubation,   10.677 per cent.

Hoppe-Seyler found that during the first 10 days of incubation almost 22 per cent. of the lecithines had disappeared, and that at the end of 17 days the lecithine-content was almost as great as the amount found in the yolk of the normal egg. At that period his investigations stopped.

As has been stated in the present work, the products of incubation were obtained and studied at the period of maturity of the living organism.

On the twenty-first day of incubation the chicken was removed from the shell. The organism of the bird was mature; every portion of the egg constituents had become converted into living substance. The bird was within one day of leaving the shell. The substance of the bird was prepared for analysis by cutting up wholly, including the flesh, bone, intestines and feathers; no particle being excluded. The extraction of the flesh and bone of bird with alcohol and ether was conducted according to the method already given.

III.— *Term of Incubation.*

Egg.	Weight of Egg.	Pyrophosphate whose source was Mineral.	Organic.	Lecithines in Egg.
No. 1.	65 grams.	0.2515 gram.	0.0793 gram.	0.88 per cent.
No. 2.	64	0.2325	0.1000	1.13

Mean of two examples = 1.00

So far the tables have shown the different proportions of lecithines found in the products at the end of each of the several terms of incubation. But in proportion as the phosphorus contained in the form of lecithine disappeared from the organism, in the same proportion the phosphates, or mineral phosphorus, were found to increase. The following table gives the actual proportions of phosphorus which were found relatively in the mineral and organic forms at the several terms of incubation.

Material.	Organic Phosphorus. Pyrophosphate.[1]	Per cent.	Mineral Phosphorus. Pyrophosphate.	Per cent.
Natural Egg	0.1677 gram =	58.5	0.1188 gram =	41.5
No. 1 Incubation	0.0931 =	37.1	0.1567 =	62.9
No. 2 Incubation	0.1072 =	43.0	0.1421 =	57.0
No. 3 Incubation	0.0896 =	27.0	0.2419 =	73.0

[1] The determinations of pyrophosphate were made by T. C. Trecot.

The analytical data contained in the above table show that, during the period of development of the embryo, as indicated by the several terms at which the process of incubation was checked, the phosphorus had become eliminated from the molecule in which it was present in the natural egg, and incorporated within a mineral body, appearing as a phosphate. That result indicates a reversion of the mode of change which was observed to occur in the vegetable organism under the action of the processes of germination. It was there established that the mineral phosphorus contained in the organism of seeds was converted from the mineral into the organic form, the phosphates being thus utilised in the formation of lecithines. The organism of the chicken during the period of its initial development breaks up the lecithine bodies, and uses the phosphorus in the formation of bone.

In the formation of the phosphate, which is the chief substance of bone, there are two other sources from which very minute portions of phosphorus might be drawn, *viz.* the albuminoid bodies containing phosphorus, the so-called nucleins, and the shell of the egg, which latter would be expected to furnish an appreciable portion of phosphate. The data obtained, however, from the analysis of the shell indicate that it could not contribute more than a trace of phosphorus (although considerable calcium) to aid the animal organism in the formation of bone. The mean of analysis of three shells gave only 0.014 gram pyrophosphate, or 0.16 per cent. of the weight of the shell. It is thus clear that the portion of phosphorus set free by the action of the animal ferments upon the inner surface of the shell during the period of incubation must be so small as not to enter into the present calculations.

It is necessary to conclude that the lecithine bodies furnish the phosphorus which is utilised by the organism in the formation of bone. This conclusion rests not only upon the high percentage of lecithines contained in the natural egg, but also upon the observation that the gradual increase of mineral phosphorus which marks the development of the embryo is accompanied by a proportional decrease in the phosphorus present as lecithine.

The lecithines are a source of the phosphorus required by the animal organism in the formation of bone. These bodies are also a medium by which the phosphorus present in vegetable organisms is received by the animal organism. Most vegetable growths

contain lecithines, and consequently the latter are consumed in animal diet.

The data obtained in the present studies contribute certain indications which bear upon the question: Are the lecithines found in the animal organism such as have been taken up in vegetable food as lecithines, or are they formed by the organism from other bodies containing phosphorus?[1] Returning to the vegetable part of the investigations, it was observed that the phosphates present in the natural seed furnished the phosphorus which was utilised by the embryo plantlet in the formation of lecithines. It was also indicated that the mineral phosphates taken up by the plant in aqueous solution from the earth, and which are seen in the tissues of the plant in crystallised form by use of the microscope, are the source and reserve-material out of which the lecithines are formed, and that the mineral phosphorus is thus first converted into a member of an organic molecule before being incorporated by the plant organism.

In the second part of the work it has been shown that the animal organism uses the lecithine bodies as the source of phosphorus required in the formation of bone. It was also indicated in the examination of the incubation-products of the second term of development that the embryo organism of the chicken had converted a portion of the mineral phosphorus originally found in the egg into lecithine phosphorus, which latter underwent a reorganisation and was utilised by the organism as a constituent of bone. For, as it has previously been maintained, it was extremely improbable, and in the reverse direction of the mode of physiological development, that any portion of an ultimate constituent of the organism should be disintegrated. Consequently, the source of the phosphorus contained in the increment of lecithines found in the incubation-products specified, and found also by Professor Hoppe-Seyler at the same period of development of the embryo, was the original phosphates present in the normal egg.

It has thus been shown that the animal organism possesses the power of converting the phosphorus of mineral phosphate into the phosphorus of lecithine, and also of breaking up those lecithines, eliminating the phosphorus and engaging it as a constituent of bone. And by the data obtained it has been shown that the

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[1] See Handbuch der physiol. Chemie, G. Bunge, S. 82.

lecithines found in the animal body may have been formed by the organism within itself, out of mineral phosphates.

It has been shown by A. Bokáy[1] that the lecithine bodies contained in food are very rapidly resolved by the animal ferments into fatty acids, cholin and phosphorus glycerine. It is, then, highly improbable that any portion of the lecithines escapes dissolution under the action of alimentary solvents, and that any part of the lecithines found in the brain and nerve system, and in the several secretions of the animal body, is received and incorporated directly from animal diet. The lecithines taken up by the animal from milk and vegetable foods, and which, it has been shown, are resolved rapidly into the given decomposition-products, doubtless furnish the phosphorus required in the formation of bone before and after the birth of the young animal. On the other hand, it has been shown that the lecithines found in the several regions of the animal body are synthetic products of the organism, the phosphorus being derived from the mineral phosphates taken up by the system in food.

The investigations of Prof. Miescher,[2] which have come to the notice of the author since the present work was begun, led to conclusions which support and are supported by the data which have been recorded. It is known that salmon fish, previous to the period of propagation, move from sea water up into the fresh streams of rivers. The duration of the breeding season extends over several months. During that season the fish consume no food, the alimentary canal always being found empty. Consequently it was observed that the substance required by the organism of the fish for the physiological processes incident to the production of young must be drawn from given regions and materials of the organism of the fish itself. Miescher, in his studies, showed by comparative determinations that the increase in the substance and weight of the ovary was at the expense of a proportional decrease in the weight of the muscular tissue. He observed also that the ova are very rich in nuclein and particularly lecithines, but the muscular tissue extremely poor in these bodies. The tissues of the muscles, however, were very rich in phosphorus, which was present in the form of phosphates. Miescher

[1] Ztschr. physiol. Chem. **1**, S. 158; 1887.
[2] "Statistische und biologische Beiträge zur Kenntniss vom Leben des Rheinlachses." Archiv für Anat. und Physiol., 1881. See note, page 195.

thus came to the conclusion that the lecithines found in great amount in the ova were formed by the organism out of the proteids, fats and phosphates contained by and forming the muscular tissue.

The investigations have shown, finally, that the lecithines exercise the function of receiving phosphorus from minerals and bestowing it in the processes of the animal organism in the formation of bone. These bodies are thus a medium through which the element performs its movements and circulation from the mineral, through the vegetable, and into the animal kingdom.

VII.—NOTES ON XYLOSE.

By W. E. Stone and W. H. Test.

The extraction from vegetable tissues of materials which upon hydrolysis yield one or both of the pentose sugars is familiar to students of the carbohydrates. These materials, to which the general name pentosans has been assigned, seem to be abundant. By boiling many vegetable substances with a dilute alkali, such as sodic or calcic hydrate, the pentosans go into solution, from which they may be precipitated by acidulation and addition of alcohol. In this manner Allen and Tollens obtained a substance from wheat-straw from which xylose was easily made by inverting with dilute sulphuric acid.[1] Such a process is, however, an uninviting task when attempted with the ordinary laboratory appliances, owing to the large amount of material required for a small amount of product.

In the manufacture of paper from straw, the straw is boiled for some hours with quick-lime, or, according to an improved process, the straw and quick-lime are placed in large rotating digesters and subjected to the action of steam under high pressure for some hours. From the paper-maker's standpoint this bleaches and disintegrates the fiber of the straw. After the digestion is complete the alkaline liquor is discharged. We have found this

[1] Ber. d. chem. Ges. **23**, 137.

extract a convenient material from which to obtain xylose, as the following notes indicate.

The liquor, after allowing suspended materials to settle, was clear and of a yellowish brown color, with a decided alkaline reaction. The specific gravity by Mohr's balance was 1.215. By titration with half-normal hydrochloric acid different samples showed an alkalinity equivalent to 2–2.5 per cent. of calcium oxide. Upon evaporating 100 cc. in a platinum dish, a thick viscous mass remained which with difficulty could be brought to a constant weight. This residue amounted to 3.95 per cent. of the liquor. By ignition 30.77 per cent. remained, leaving 69.23 per cent. of the solids as organic matter.

Some of the liquor which had been concentrated to one-half its volume by evaporation, was acidulated with hydrochloric acid and received one and one-half volumes of 95-per cent. alcohol, when a dense flocculent precipitate was thrown down. This was dissolved in water and reprecipitated with alcohol three times. Finally the precipitate was strained, pressed dry and placed in large desiccators over sulphuric acid. The material was of a pearly gray color, amorphous, with a tendency to blacken if left exposed to the air. It was, as its further examination showed, the mother-substance of xylose or xylan. From 32 liters of the straw liquor we obtained about 300 grams of xylan. In spite of the attempts at purification it still contained 8.57 per cent. of ash, of which 6.13 per cent. was calcium oxide.

Upon distillation with hydrochloric acid and titration of the distillate with phenylhydrazine in the manner proposed by one of us,[1] the xylan yielded in different determinations 45.5 and 47.1 per cent. of furfurol.

Some attempts were made to ascertain if it were possible to hydrolyse this material by the use of small amounts of acid as has been done by Wohl in the case of inulin ;[2] but different modifications of Wohl's method failed to give satisfactory results, and we judge that xylan is far less sensitive to hydrolytic action than inulin.

Hydrolysis was therefore effected in the usual way by heating during eight or ten hours with eight parts of 2-per cent. sulphuric acid. The acid solution was neutralised, evaporated to a syrup, extracted with alcohol and the alcoholic solution again concen-

[1] J. Anal. and Appl. Chem. **5**, No. 8.   [2] Ber. d. chem. Ges. **23**, 2084.

trated to a syrup which soon crystallised. After purification the product weighed 35 grams, or a little more than 1 per cent. of the liquor employed and over 10 per cent. of the xylan treated.

The product was identified as xylose by its specific rotation $=$ $(a)_D = +18.4°$, and by the phenylhydrazine compound which melted at 158° and was distinctly laevo-rotatory.[1] It also possessed the other less characteristic properties of xylose.

A second portion of the straw-liquor has been hydrolysed directly without the preliminary precipitation and purification of the xylan, and has given equally good results. It presents, therefore, a convenient source of xylose, the employment of which is preferable to the preparation of the crude material in the laboratory.

The multi-rotation of xylose has been studied by Tollens and Parcus,[2] and we are able to confirm their results by observations upon this material. Two grams of the purified xylose were dissolved in cold water and quickly brought into the polariscope. Only four minutes elapsed between the addition of the water to the sugar and the first reading. The rotatory power decreased very rapidly, as is shown by the following five readings, taken as rapidly as they could be made and recorded:

$$
\begin{array}{llll}
1. & +14° & 2' = (a)_D & 71.65° \\
2. & +13° & 56' = " & 69.65° \\
3. & +13° & 12' = " & 66.00° \\
4. & +12° & 24' = " & 62.00° \\
5. & +12° & 8' = " & 60.65°
\end{array}
$$

The readings were begun at 6.30 A. M. and continued at hourly intervals until they became constant. The decrease, which at first was very rapid, was practically at an end after three hours.

Four minutes after solution:

6.30 A. M., $(a)_D = 71.65°$			12.30 P. M., $(a)_D = 18.95°$		
7.30 " " $= 27.76°$			1.30 " " $= 18.85°$		
8.30 " " $= 21.22°$			2.30 " " $= 18.75°$		
9.30 " " $= 18.95°$			3.30 " " $= 18.40°$		
10.30 " " $= 18.95°$			4 30 " " $= 18.40°$		
11.30 " " $= 18.95°$					

[1] Ber. d. chem. Ges. **23**, 355.   [2] Ann. Chem. (Liebig) **257**, 175.

ON AMIDOPHOSPHORIC ACID.

By H. N. Stokes.

By replacing the hydroxyls of orthophosphoric acid success-
ively by amido groups, three amides may be derived, namely,
amidophosphoric acid, $PO.NH_2.(OH)_2$, diamidophosphoric acid,
$PO.(NH_2)_2.OH$, and phosphoryl triamide, $PO(NH_2)_3$, and from
these, by abstraction of water or ammonia, an imido acid,
$PO.NH.OH$, an imido amide, $PO.NH.NH_2$, and a nitrile, $PO.N$.
Of these, amido- and diamidophosphoric acids have not yet been
described. In the dictionaries of Fehling [1] and of Ladenburg [2]
the formula $PO.NH_2.(OH)_2$ is given to a body described by
Schiff [3] and called by him *phosphaminsaeure*. This rests on an
error of the compilers, as Schiff gives to his acid the formula
$PO.NH.OH$, with which his analyses agree, while they differ
widely from that of amidophosphoric acid. Moreover, as will be
shown, amidophosphoric acid is a body of entirely different
properties.

Schiff [4] also describes the triamide, $PO(NH_2)_3$. Although his
analyses agree quite well with this formula, the existence of the
body is called in question by Gladstone, [5] who, in repeating Schiff's
method of preparation, treating phosphorus oxychloride with dry
ammonia, was unable to replace the third chlorine atom at any
temperature below that at which further decomposition occurs
(above 300°). The correctness of the formula $PO.NH.OH$
assigned by Schiff to his phosphamic acid is also questioned by
Gladstone and Holmes, [6] who point out the general resemblance
of its properties, as described, to those of pyrophosphodiamic acid,
obtained by them. They regard it as a mixture of the latter with
metaphosphoric acid. The identity of Schiff's acid with pyro-
phosphodiamic acid (diamidopyrophosphoric acid) has also found
acceptance in some handbooks. [7]

The imido amide, $PO.(NH).NH_2$, was described by Gerhardt [8]
under the name phosphamide, and was obtained by treating phos-

[1] Neues Handwörterbuch der Chemie **5**, 423.   [2] Handwörterbuch der Chemie **9**, 100.
[3] Ann. Chem. (Liebig) **103**, 168.   [4] Ann. Chem. (Liebig) **101**, 300.
[5] Journ. Chem. Soc. [2] **7**, 18.   [6] Journ. Chem. Soc. [2] **2**, 229, 235.
[7] Gmelin-Kraut: Handbuch der anorg. Chemie **1**, 2 Abth. 529 ; Graham-Otto: Anorg. Chem.
(Michaelis) **2**, 401.
[8] Ann. chim. phys. [3] **18**, 188.

phorus pentachloride with dry ammonia and then with water. Its nature has not been questioned.

The body PO.N, described by Gerhardt[1] as biphosphamide, by Schiff[2] as monophosphamide, and by Gladstone[3] as phosphonitryle, is the final product of heating the triamide, the imidoamide or the amido chlorides. Its constitution is not known, but is probably much more complex than is represented by the formula given.

In addition to the above, Gladstone and Holmes[4] have obtained a series of complex amides, derivable from pyro- and tetraphosphoric acids.

The difficulty in preparing amido orthophosphoric acids lies in part in the impossibility of regulating the decomposition by water or acids of the products of the action of ammonia on phosphorus pentachloride and oxychloride. Gerhardt's imidoamide and Schiff's triamide seem to be capable of giving ammonia and phosphoric acid only ; at least no mention is made of intermediate products. The bodies derived from phosphorus oxychloride by partial replacement of chlorine by amido groups are so decomposed by water as to give the amidopyrophosphoric acids of Gladstone, and further action results in the separation of ammonia before the pyrophosphoryl group is broken up. The reason for this, as will be seen below, lies in the great ease with which amidophosphoric acid passes over into ammonium phosphate. As phosphorus pentoxide is a derivative of pyrophosphoric acid, it is not to be expected that it would give orthophosphoric amides with ammonia.

I have overcome these difficulties in part, by acting with ammonia on phosphoric ethers, and in this way have obtained the primary amide, $PO.NH_2.(OH)_2$. Attempts to obtain other amides by the same method are in progress.

By dissolving the chloride of diphenylphosphoric acid, $PO.Cl.(OC_6H_5)_2$, in alcohol, and adding alcoholic ammonia, diphenylamidophosphate, $PO.NH_2.(OC_6H_5)_2$, a beautifully crystalline substance, is at once formed. This, on saponifying with ammonia or baryta, gives phenylamidophosphoric acid, $PO.NH_2.(OC_6H_5).(OH)$, and with caustic potash or soda, amidophosphoric acid. The free acid, obtained by decomposing the lead salt by sulphur-

[1] Ann. chim. phys. [3] **18,** 188.

[2] Ann. Chem. (Liebig) **101,** 304.

[3] Journ. Chem. Soc. [2] **7,** 18.

[4] Quar. Journ. Chem. Soc. **3,** 353; Journ. Chem. Soc. [2] **2,** 225; [2] **4,** 1, 290; [2] **6,** 64, 261; [2] **7,** 15.

etted hydrogen, and precipitating with alcohol, is a well characterised body, forming fine microscopic crystals. It forms two series of salts, acid and neutral, of which the acid salts are invariably, the neutral often, crystalline, and in many cases the forms are characteristic. Boiled in aqueous solution, either alone or with an acid, it decomposes almost instantly into ammonia and orthophosphoric acid. Its cold aqueous solution may be kept a short time without much decomposition, but quickly passes into primary ammonium orthophosphate. Dilute mineral acids in the cold effect the change much more rapidly, but in either case the first product is not orthophosphoric acid, but an acid or mixture of acids giving white amorphous precipitates with silver nitrate. At 100° the dry acid passes without loss of weight into an ammonium salt, giving a white silver salt. This is possibly metaphosphate, or a mixture of the different metaphosphates,

$$PO\begin{matrix} NH_2 \\ OH \\ OH \end{matrix} = PO_3(NH_4),$$
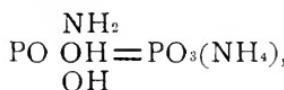
but the nature of the product has not yet been established. The acid salts on heating give off ammonia and leave metaphosphates. Such of the neutral salts as contain crystal water pass first into ammonium salts, and on further heating into pyrophosphates. The neutral silver salt, which is anhydrous, is an exception. At 180° it gives off one half its nitrogen as ammonia, apparently forming a very stable *pyrimidophosphate*,

$$NH\begin{matrix}< \end{matrix}\begin{matrix} PO(OAg)_2 \\ PO(OAg)_2 \end{matrix},$$
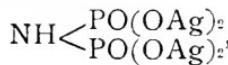
which stands a red heat without further change, or at least without loss of weight. Other salts which are especially characteristic are the acid sodium salt, almost insoluble in water, and the neutral magnesium salt, isomeric with crystallised ammonium magnesium phosphate. In the absence of any experimental proof of the contrary, the constitution of the acid is regarded as $PO\begin{matrix} NH_2 \\ (OH)_2 \end{matrix}$, in accordance with the usually assumed structure of acid amides, rather than as $P(NH)(OH)_3$, in harmony with the most recent views on the nature of organic amides.

DESCRIPTIVE PART.

Diphenylamidophosphate, $PO\genfrac{}{}{0pt}{}{NH_2}{(OC_6H_5)_2}$.—1 mol. wt. phosphorus oxychloride and 2 mol. wts. phenol are boiled in a flask fitted with return condenser until no further evolution of hydrochloric acid occurs. The product is a mixture of $PO(OC_6H_5)_3$, $PO.Cl.(OC_6H_5)_2$, $PO.Cl_2.(OC_6H_5)$ and unchanged oxychloride. It is not necessary to isolate the diphenylphosphoric chloride. The liquid is diluted with absolute alcohol, and alcoholic ammonia is added slowly, with cooling, to alkaline reaction. The product is mixed with several volumes of water, whereby ammonium chloride dissolves and crystalline amidophosphate separates, mixed with oily phenyl-phosphates. This is sucked out in a funnel as far as possible, washed with water, dried on porous plates to remove the oil, again washed, dried and recrystallised two or three times from alcohol, or better, chloroform. The yield is about 35 per cent. of the theoretical.

	Calculated for $PO.NH_2.(OC_6H_5)_2$.		Found.	
P	12.46	...	12.37	...
N	5.67	5.70	5.64	5.67

Phosphorus was determined as magnesium pyrophosphate after evaporating first with alkali, then with acid; nitrogen as ammonia after evaporating with hydrochloric acid; both as ammonium chloroplatinate and by titration, after distilling.

The ether fuses at 148°, and on cooling solidifies to a crystalline mass with a surface of brilliant facets. At 180° there is a very slow evolution of ammonia and phenol, which becomes quite rapid at 230°, when it is accompanied by sublimation of unchanged substance. The non-volatile product of decomposition is first an oil, later a solid substance containing phosphorus.

Phenylamidophosphoric acid, $PO\genfrac{}{}{0pt}{}{NH_2}{OC_6H_5}{OH}$.—The free acid could not be obtained in the solid state. On decomposing the lead salt in the cold with sulphuretted hydrogen a solution is obtained which is not precipitated by alcohol. On evaporating *in vacuo* over sulphuric acid, the acid takes up water and is converted into the acid ammonium salt of phenylphosphoric acid, which contains only traces of amido acid, which were isolated as the silver salt described below.

Acid ammonium phenylphosphate is easily soluble in water, and crystallises in long prisms. It also crystallises from alcohol, in which it is difficultly soluble, as pearly rhombic plates or flat needles, fusing at $140°$–$145°$ with decomposition. Silver nitrate gives a precipitate of radiating flat prisms consisting of the *neutral silver salt*, (*a*) which is anhydrous. By neutralising the filtrate with ammonia a further precipitate of the same salt (*b*) is obtained.

	Calculated for $PO_{OC_6H_5}^{(OAg)_2}$.	Found.	
		(*a*)	(*b*)
Ag	55.64	54.88	55.44

Phenylphosphoric acid therefore resembles phosphoric acid in that its acid salts give directly the neutral silver salt, and differs from amidophosphoric acid, which gives either acid or neutral silver salt according as acid or neutral salt be used as precipitant.

Ammonium phenylamidophosphate, $PO \begin{matrix} NH_2 \\ OC_6H_5 \\ ONH_4 \end{matrix}$, obtained by saponifying the diphenyl ether with aqueous ammonia, is easily soluble in water, and the solution may be evaporated without decomposition.

Silver phenylamidophosphate, $PO \begin{matrix} NH_2 \\ OC_6H_5 \\ OAg \end{matrix}$, from the ammonium salt, after recrystallising from water, forms scales or long, narrow, pointed plates of pearly lustre. It is difficultly soluble in cold, moderately in boiling water, and has a strong tendency to separate as a crystalline scum on the surface. It is unaffected by light.

	Calculated for $PO(NH_2)(OC_6H_5)(OAg)$.	Found.		
P	11.09	...	11.11	...
N	5.02	...	5.08	...
Ag	38.53	38.31	...	38.19

Barium phenylamidophosphate is formed by boiling the ether with baryta water until nothing crystallises out on cooling, and removing the excess of baryta by carbon dioxide. It forms scales, is quite soluble in water, and resembles the silver salt in forming a crystalline scum on the surface.

Lead phenylamidophosphate, from the barium salt by lead acetate, forms brilliant scales, nearly insoluble in water.

Amidophosphoric acid, $PO \begin{matrix} NH_2 \\ (OH)_2 \end{matrix}$.—The alkali salts of this acid are readily obtained by saponifying the ether with a strong solu-

tion of caustic potash or soda. The chief difficulty in obtaining them pure is in separating them from the small quantity of phosphate formed at the same time. In the case of some of the salts this may be effected by methods mentioned below. The conversion into phosphate by boiling alkali is very slow. A weighed amount of ether was boiled with concentrated caustic potash, and the ammonia determined in the distillate by titration. An hour's boiling showed a decomposition of only three per cent.

Acid potassium amidophosphate, $PO\genfrac{}{}{0pt}{}{NH_2}{OK.OH}$ — If a lump of caustic potash be placed on some diphenyl ether and a few drops of water be added, a somewhat violent reaction occurs. On boiling with an excess of concentrated caustic potash, the saponification is complete in ten minutes. The oily solution is acidified with strong acetic acid, care being taken to keep it cool with icewater. On adding several volumes of alcohol, the acid salt is at once precipitated. It is purified by washing with alcohol, dissolving in a little water and reprecipitating by alcohol. It cannot be recrystallised from hot water, as its solution is rapidly converted by heating into acid potassium ammonium phosphate. A weighed amount of acid potassium salt was dissolved in water and boiled ten minutes; $\frac{1}{10}$ n. caustic soda was added in excess, and the solution again boiled to remove ammonia. The loss of alkalinity due to the escape of ammonia indicated that by ten minutes' boiling, ninety-eight per cent. of the amide was converted into ammonium salt. The same change occurs in a few days in the cold aqueous solution. The salt forms six-pointed stars, or sometimes rhombohedra, readily soluble in cold water, insoluble in alcohol. Its solution is neutral towards litmus, methyl orange and phenolphthalein. On ignition it gives off ammonia and leaves potassium metaphosphate.

The analysis of two air-dried preparations (*a* and *b*) gave—

	Calculated for $PO.NH_2.OK.OH$.	Found.	
		a.	*b.*
P	22.96	22.76	...
N	10.39	10.26 10.20	10.35

The loss on ignition gave—

| | Calculated for $PO.NH_2.OK.OH$ | Found. |
| NH_3 | 12.61 | 13.83 |

The excess found is due in part to a small amount of water which the salt retains, in part to a little acid potassium ammonium phosphate which cannot be removed by precipitating with alcohol. The amount of ammonium salt may be determined by distilling off the ammonia with alkali solution, and determining it in the distillate, making a slight correction for the decomposition of the amide itself as above determined (3 per cent. per hour). In this way the amount of ammonium salt in preparation (*a*) was found to be 4.75 and 5.10 per cent., in (*b*) 4.15 per cent. As the acid potassium salt is used for preparing other salts, this small amount of phosphate has to be taken into consideration, as the latter would otherwise be contaminated with phosphate. Its presence may be obviated by methods below mentioned.

Neutral potassium amidophosphate is extremely soluble in water, and not appreciably decomposed by boiling.

Acid sodium amidophosphate, $PO\begin{cases}NH_2\\ONa\\OH\end{cases} + xH_2O(?)$.—This is prepared by boiling the ether ten minutes with strong caustic soda, cooling and acidifying with acetic acid. It separates at once without adding alcohol, as a crystalline powder, which is washed with dilute alcohol, dissolved in ammonia, and reprecipitated by acetic acid or carbon dioxide. It forms a heavy sandy powder consisting of well defined crystals belonging to the hexagonal system, occurring sometimes as hexagonal plates or prisms without pyramids, occasionally as very symmetrical double pyramids without prism surfaces. It is scarcely soluble in cold water, insoluble in alcohol. If boiled with water it dissolves and is at once converted into acid sodium ammonium phosphate. The same change occurs slowly at ordinary temperature under water. Like all other amidophosphates, it is instantly converted into phosphoric acid by warm dilute acids. On ignition it loses ammonia, and leaves a vitreous residue of sodium hexametaphosphate. It contains small but varying amounts of water. The analysis of one preparation gave—

	Calculated for $PO.NH_2.ONa.OH + \frac{1}{2}H_2O$.	Found.	
P	25.11	25.08	
N	11.36	11.49	11.34
Residue ($NaPO_3$)	82.54	82.43	

Other samples contained less water. This water is accounted for in part by the presence of a small amount of acid sodium ammonium phosphate, but the latter, when determined as in the acid potassium salt, was found to be only 2–2.5 per cent., while the whole amount of water present, if assumed to be in the form of ammonium salt, would make the amount 16.8 per cent. The water is therefore present mainly as such. It does not act on the amido group at 100°, as the quantity of ammonia expelled by alkali after heating at this temperature is not increased, and there is no loss of weight. At 150° it reacts, converting a portion of amide into ammonium salt, which at the same time loses ammonia, the residue being found to contain less nitrogen. The acid sodium salt dissolves rather difficultly in excess of ammonia, probably forming the sodium ammonium salt; from this solution it is reprecipitated by carbon dioxide, or even by expelling the ammonia by an air current or spontaneous evaporation. In this respect it resembles the neutral phosphates containing ammonia.

Neutral sodium amidophosphate, $PO\frac{NH_2}{(ONa)_2}$, is readily made by treating caustic soda solution with excess of acid salt, the excess remaining undissolved. It forms bunches of needles or prisms, extremely soluble in water, but not deliquescent. By the action of carbon dioxide, even that in the air, it is decomposed into acid salt and sodium carbonate. Alcohol precipitates it as a syrup from aqueous solution.

Acid lithium amidophosphate is precipitated by lithium chloride from a strong solution of the acid potassium salt, in the form of difficultly soluble crystalline granules. On boiling it is converted into phosphates of lithium.

Acid ammonium amidophosphate is formed by decomposing either the acid or neutral silver salt with ammonium sulphide and precipitating by alcohol. It forms a beautiful network of needles, crossing at angles of 60°, and is very soluble in water, and permanent in the air. As it is formed by precipitating an ammoniacal solution by alcohol, it appears that the neutral salt is very unstable, if capable of existence.

Potassium ammonium amidophosphate is precipitated by alcohol from an ammoniacal solution of the acid potassium salt as a syrup, which is decomposed by washing with alcohol into acid potassium salt and ammonia.

Acid hydroxylamine amidophosphate, obtained by precipitating a moderately strong solution of the acid potassium salt with hydroxylamine hydrochlorate, is difficultly soluble in water, and forms brilliant rhombic plates and prisms.   Its crystallising power is greater than that of any other salt obtained.   A neutral salt could not be prepared.

The preparation of salts of the earths and heavy metals from the acid potassium salt is interfered with by the latter being contaminated with a small amount of phosphate.   The contamination of the precipitate in the case of the salts is best avoided by adding to the ice-cold solution of the acid potassium salt, before precipitation, a very little dilute nitric acid, which effectively holds all phosphate in solution.   In making neutral salts, it is not so easy to get rid of the phosphate; the ways in which this was accomplished are given in special cases below.

Acid barium amidophosphate, $\left(PO \begin{matrix} NH_2 \\ OH \\ O- \end{matrix} \right)_2 Ba + 2\frac{1}{4}H_2O$, is obtained by adding to an ice-cold solution of acid potassium salt, faintly acidified with nitric acid, barium chloride in excess.   It thus forms a supersaturated solution, which crystallises only on rubbing with a glass rod.   The precipitate is washed with a little water and alcohol. It forms groups of radiating microscopic plates, and once formed is quite difficultly soluble in water.   On boiling its solution, a scaly crystalline precipitate of acid barium phosphate, $BaHPO_4$, at once forms.   It contains about $2\frac{1}{4}$ mols. crystal water, the greater part of which is lost at $100°$, but this cannot be directly determined, owing to its tendency to pass into ammonium salt with loss of ammonia.   On ignition it fuses to a glass of barium hexametaphosphate.

	Calculated for $Ba(PO_3NH_3)_2 + 2\frac{1}{4}H_2O$.	Found.
Loss $(2NH_3 + 2\frac{1}{4}H_2O)$	20.17	19.82

The residue gave—

	Calculated for $Ba(PO_3)_2$.	Found.
Ba	46.43	47.12
P	21.03	21.38

Neutral barium amidophosphate, $PO \begin{matrix} NH_2 \\ O \\ O \end{matrix} > Ba + H_2O$.—By mixing a dilute solution of acid potassium salt with ammoniacal

barium chloride solution, and filtering quickly from the small amorphous precipitate of barium phosphate, the salt soon crystallises. It forms very characteristic hard and brittle rhombic plates, often with truncated angles, often superposed in coincident or partly turned position, sometimes also as fine prisms with many sharply defined faces. It is unchanged at 100°, but at 150° the crystal water is taken up to form ammonium salt, which at once loses ammonia, forming acid barium phosphate, which on ignition leaves a residue of pyrophosphate, giving off but little ammonia.

$$\text{Calculated for } PO\underset{O}{\overset{NH_2}{>}}Ba + H_2O.$$

	Calculated	Found.
Loss of 1 mol. NH_3 at 150°	6.80	6.84
Total loss on ignition, $NH_3 + \frac{1}{2}H_2O$	10.40	10.70

The residue gave—

	Calculated for $Ba_2P_2O_7$.	Found.
Ba	61.17	61.80
P	13.84	14.44

The salt is very difficultly soluble in water. Its solution, or the liquid from which it has not yet crystallised, gives on boiling, even in the presence of an excess of ammoniacal barium chloride, a scaly precipitate of acid barium phosphate.

	Calculated for $BaHPO_4$.	Found.
Loss on ignition $\frac{1}{2}H_2O$	3.86	4.65

The residue gave—

	Calculated for $Ba_2P_2O_7$.	Found.
Ba	61.16	61.76

The salt shows a peculiar behavior when formed in the presence of strong ammonia. By mixing a solution of the acid potassium salt with strongly ammoniacal barium chloride, an amorphous precipitate is formed, which dissolves (excepting traces of phosphate) on adding water. Strong ammonia reprecipitates it, and more water dissolves it; this process may be repeated several times. The solution soon deposits crystals of the neutral salt, and the precipitate itself soon turns to scales of the same substance. Filtered off and washed with ammonia, it gave on analysis figures corresponding to those of the neutral salt.

Acid calcium amidophosphate, obtained like the barium salt, is much less soluble than the latter, and forms spherical aggregations of needles.

Neutral calcium amidophosphate is formed like the neutral barium salt, but is much less soluble. Its crystallising power is also much less. From very dilute solutions it separates gradually in the form of microscopic groups of flat-pointed prisms; from concentrated solutions as an amorphous precipitate which does not become crystalline, while from solutions of intermediate strength it is at first amorphous but gradually becomes crystalline.

Acid magnesium amidophosphate, $\left(\begin{array}{c} NH_2 \\ POOH \\ O- \end{array}\right)_2 Mg + 3\frac{1}{4}H_2O.$—
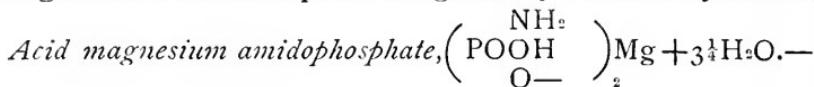
On mixing an ice-cold strong solution of acid potassium salt, acidified slightly with nitric acid, with magnesium chloride, nothing separates, even after many hours. On rubbing with a glass rod, crystallisation starts at once. Once separated it is almost insoluble in water, and forms microscopic granules consisting of radiating needles or prisms. It is insoluble in ammonium chloride. At 100° it retains 2 mols. water; on ignition it gives off ammonia and water, and leaves magnesium metaphosphate.

	Calculated for $Mg(PO_3NH_3)_2 + 3\frac{3}{4}H_2O.$	Found.
Loss $(2NH_3 + 3\frac{1}{4}H_2O)$	33.71	33.86

The residue gave—

	Calculated for $Mg(PO_3)_2.$	Found.
Mg	13.18	12.85
P	34.10	33.88

Neutral magnesium amidophosphate, $POO\begin{array}{c} NH_2 \\ \diagdown \\ O \end{array} Mg + 7\,H_2O.$—
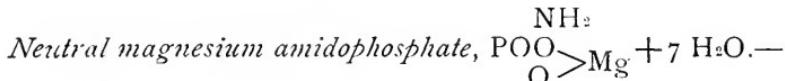
This salt has the same empirical composition as crystallised ammonium magnesium phosphate, $MgNH_4PO_4 + 6H_2O$, but differs entirely in its properties. It forms at once on adding magnesia mixture to a solution of acid potassium salt, or better, by precipitating neutral sodium salt with a magnesium salt. Any phosphoric acid present is first thrown down by a little of the precipitant, either as magnesium or magnesium ammonium phosphate; even when phosphoric acid is in excess it is completely thrown down by magnesia mixture before any amidophosphate forms, and the change can easily be followed by observing the crystals under the microscope. From solutions containing ammonium chloride (as when magnesia mixture is used) it crystallises

in very characteristic plates, often nearly rectangular, but more frequently with truncated angles, forming oblong octagonal plates. In the absence of ammonium salts it forms thick prisms, in either case easily distinguishable from ammonium magnesium phosphate. It is difficultly but perceptibly soluble in water, and quite readily in dilute ammonium chloride solution, and may be separated from any accompanying ammonium magnesium phosphate in this way. From its aqueous solution ammonia precipitates magnesium hydroxide. On boiling its aqueous solution, ammonium magnesium phosphate is at once formed. It dissolves in acetic acid; from its solution in nitric acid, alcohol precipitates acid salt. Even when free from ammonium salt, caustic potash causes more or less evolution of ammonia in the cold. Over sulphuric acid it quickly loses most of its crystal water, but the last two or three molecules are given off very slowly, and constant weight could not be obtained. At 100° it loses somewhat more than 5 mols., but this cannot be accurately determined, as at this temperature partial decomposition of the amide with loss of ammonia occurs, as shown by analysis of the residue. On ignition it leaves magnesium pyrophosphate.

	Calculated for $MgPO_3NH_2 + 7H_2O$.	Found.	
P	12.67	12.59	
N	5.73	6.53	6.27
Mg	9.79	9.77	
Loss on ignition	54.70	54.79	

Acid manganese amidophosphate, prepared like the acid magnesium salt, forms faintly pinkish microscopic crystals, or granular and lenticular forms. It contains crystal water, is difficultly soluble, and shows no tendency to form supersaturated solutions.

Neutral manganese amidophosphate, from the neutral sodium salt, is an amorphous white precipitate.

Acid zinc amidophosphate is difficultly soluble in water; soluble in acetic acid and in ammonia. It crystallises readily in small but finely-formed rhombic prisms with pyramids, or in hexagonal plates.

Neutral zinc amidophosphate is an amorphous white precipitate, perceptibly soluble in water. Both salts are converted into phosphate by boiling.

Cobalt amidophosphates. The *acid* salt forms readily from the acid potassium salt with a cobalt salt, after adding a drop of nitric

acid. It is difficultly soluble in water; soluble in ammonia, and forms pink granules. The *neutral* salt is an amorphous pink precipitate.

Nickel amidophosphates. The *acid* salt has a great tendency to supersaturation, and can only with great difficulty be made to crystallise. Once formed, it consists of minute crystalline granules, difficultly soluble in water. The *neutral* salt is an amorphous, nearly colorless precipitate, soluble in acetic acid and in ammonia.

Ferrous amidophosphates. The *acid* salt, formed as above, crystallises very readily in nearly colorless microscopic crystals, apparently of the regular system, and consisting of the dodekahedron or combinations of cube and octahedron. It is nearly insoluble in water or ammonium chloride; soluble in ammonia. The *neutral* salt is a dirty greenish, amorphous precipitate, soluble in much water, in acetic acid and in ammonia.

Ferric amidophosphates. Both acid and neutral alkali salts give, with a neutral solution of ferric chloride, white, amorphous precipitates, soluble in excess of amidophosphate and in ammonia, insoluble in acetic acid.

Aluminium amidophosphate. Neutral sodium salt gives, with alum, a white, amorphous precipitate, completely soluble in ammonia.

Chromic amidophosphate, from neutral sodium salt, is a very nearly colorless amorphous precipitate, soluble in ammonia on warming.

Cupric amidophosphates. The *acid* salt crystallises in rosettes and dumb-bell-like forms, nearly insoluble in water. The *neutral* salt is an amorphous precipitate, slightly soluble in water, and converted into phosphate by boiling.

Mercuric amidophosphates. Neither acid nor neutral salts are precipitated by mercuric chloride. On boiling, mercuric phosphate is formed.

Cadmium amidophosphates. By mixing solutions of acid potassium amidophosphate and cadmium chloride, crystalline precipitates somewhat soluble in water are obtained. These differ in form according as one or the other reagent is in excess; with excess of cadmium chloride a double salt is formed, which gives off ammonium chloride on heating.

Lead amidophosphate. Acid potassium salt and lead acetate give a precipitate consisting of groups of radiating plates, slightly soluble in water, presumably acid salt.

Acid silver amidophosphate, $PO \begin{smallmatrix} NH_2 \\ OAg \\ OH \end{smallmatrix}$.—This may be obtained
by precipitating the acid potassium salt with silver nitrate, but, thus obtained, it contains too much silver (about 2 per cent.), due, perhaps, to a small amount of neutral salt or to a trace of phosphate. By previously adding a very little nitric acid to the cold solution, it is obtained pure. As it is somewhat soluble in water, the theoretical yield cannot be obtained. It is also formed by dissolving the neutral salt in cold dilute nitric acid and precipitating by alcohol, or by adding alcohol to a solution of the free acid and silver nitrate. It forms a heavy crystalline powder, consisting of short needles, or, oftener, of very thick, short, hexagonal prisms with pyramidal ends, united into groups or twins ; also, by precipitating with alcohol, as hexagonal stars. The forms are very characteristic. It is difficultly but appreciably soluble in water, easily in dilute nitric or acetic acid, and in ammonia ; from the latter solution it crystallises on evaporation. The aqueous solution is at once converted into phosphate by boiling. Light does not discolor it. The air-dried salt is anhydrous. Analysis gave :

	Calculated for $PO \begin{smallmatrix} NH_2 \\ OAg \\ OH \end{smallmatrix}$.	Found.
P	15.22	15.23
Ag	52.90	53.?5

On ignition it loses ammonia and leaves an easily fusible glass of silver hexametaphosphate.

	Calculated for $PO \begin{smallmatrix} NH_2 \\ OAg \\ OH \end{smallmatrix}$.	Found.
Loss (NH_3)	8.36	8.17

Neutral silver amidophosphate, $PO \begin{smallmatrix} NH_2 \\ (OAg)_2 \end{smallmatrix}$.—This is obtained either by adding silver nitrate and then ammonia to the filtrate from the acid salt, or (with much loss) by dissolving the acid salt in very dilute nitric acid, and adding silver nitrate and ammonia. It forms at first a turbidity, which in a few moments turns to a quickly subsiding crystalline precipitate. The ammonia must be added cautiously, and stopped as soon as the salt ceases to subside quickly. At this point a nearly white amorphous substance of unknown composition is formed, which remains in suspension, and may be redissolved by a drop of nitric acid. Further

addition of ammonia to the filtrate gives the same amorphous salt, which is faintly yellow, and rapidly blackens in the light. It may also be obtained from the neutral sodium salt, but this method is not to be recommended, as the product is slightly yellow. The best method is the first mentioned, and if very dilute solutions of acid potassium salt have been used, nearly all the acid silver salt remains in solution and can be converted into neutral salt as described. The neutral salt forms characteristic microscopic rhombic plates, with angles of nearly 60°, often united to bunches. It is colorless and unaffected by light. The crystalline powder is soft, and can thus be distinguished from the acid salt, which is gritty. It is almost insoluble in water; soluble in nitric acid, from which solution alcohol precipitates acid salt; soluble in ammonia, and deposited unchanged on spontaneous evaporation. The air-dried salt is anhydrous.

	Calculated for $PO.NH_2(OAg)_2$.	Found.	
P	9.98	10.03	9.87
N	4.52	4.51	
Ag	69.40	69.18	69.15

It remains unchanged at 150°; at 180° it loses weight, the loss corresponding to one-half the total nitrogen calculated as ammonia. On heating to constant weight at 180° —

	Calculated for $2PO.NH_2(OAg)_2 - NH_3$.	Found.
Loss,	2.74	2.82

The residue is brownish, but may be fused over the blast with but slight loss, whereby a little oxygen escapes, and a small amount of metallic silver is formed. In the above case this was weighed, and found to be only 5.61 per cent. out of a total of 69.40 per cent. The loss between 180° and red heat was 0.34 per cent., and this is exactly the amount of oxygen which would be given off by the silver oxide corresponding to 5.61 per cent. silver. The residue on ignition consists, besides metallic silver, of a yellow glass, soluble in ammonia. Probably there is formed at 180° the silver salt of *pyrimidophosphoric acid*,

$$NH \!\! <^{PO(OH)_2}_{PO(OH)_2},$$

which is not decomposed by fusion. Attempt will be made to isolate the free acid.

If the salt be heated at once over the blast, without previous heating at 180°, the decomposition is markedly different, much more metallic silver being formed.

	Calculated for ½N as NH₃.	Found.
Loss,	2.74	4.63
Free silver,	...	25.75

This amount of silver corresponds to 1.91 per cent. oxygen, which with 2.74 per cent. ammonia makes 4.65 per cent. loss, the amount actually found. The formation of silver oxide is due to the liberated ammonia, which splits off silver oxide and water, forming a higher amide. The action of dry ammonia gas on the salt is scarcely appreciable at 180°, as was found by experiment, hence the salt may be heated at this temperature without the ammonia which is given off liberating any considerable amount of silver oxide, as seen in the first case. At 200° and higher, dry ammonia forms large amounts of silver oxide and water, and therefore on heating rapidly, as in the second case, the liberated ammonia is able to act, and the large amount of silver formed is accounted for. The products of the action of dry ammonia on this salt will be described in a future article, when it will also be shown that amidophosphates may be made from neutral silver phosphate in this way. Experiments towards forming other inorganic amides by this method are also in progress.

Free Amidophosphoric Acid.

The isolation of the free acid is attended with difficulties, owing to its unstable nature. It has not yet been obtained perfectly pure, and the yield is always far below the theoretical. The silver salts may be decomposed by hydrochloric acid in the cold, and the solution precipitated by alcohol, but a deficiency of acid causes the solution to be contaminated with acid salt, and an excess destroys the amido acid completely, or at least prevents its precipitation. The decomposition of the silver salts by sulphuretted hydrogen gives better, but unsatisfactory, results. The best results are obtained by suspending the lead salt in a little ice-water, and decomposing by sulphuretted hydrogen. It is essential to have the latter in excess, as otherwise the solution contains some lead salt. The filtrate is run into four or five volumes of alcohol, whereby the acid is at once precipitated in the form of

microscopic crystals. These consist sometimes of thick plates, sometimes of forms which appear to be cubes, but which are anisotropic. It is insoluble in alcohol, easily soluble in water, the solution having a sweetish taste. It gives no precipitate with silver nitrate, unless on addition of ammonia or alcohol. It evolves no ammonia with caustic alkalies, and is easily converted into the characteristic sodium, magnesium, barium and silver salts, hence there can be no question as to its nature. It may be exposed to the air for a long time without change, but gradually alters, becoming pasty, in which condition it precipitates silver nitrate directly, and hence has become converted into an ammonium salt. The precipitate is white and amorphous, hence not phosphate. Its solution, if boiled but a moment, also gives a white silver precipitate, but, on boiling several minutes, it is completely converted into phosphate. It does not lose weight at 100°, but is slowly converted into ammonium salt, giving a white silver precipitate direct. Whether the product is one of the isomeric ammonium metaphosphates has not yet been determined. At 150° it also loses nothing, but fuses partially, and on higher heating it gives off ammonia. The silver salt from the acid which has been heated just to fusion becomes pasty under boiling water, like silver hexametaphosphate. The free acid obtained as above did not give satisfactory results on analysis, and such data are therefore postponed.

The alcoholic filtrate from the free acid contains an abundance of ammonium salts, giving amorphous, white, silver precipitates.

The action of amidophosphoric acid towards indicators is not sharp. The free acid gives acid reaction, the acid alkali salts have neutral reaction, but no sharp transitions can be obtained either with litmus, methyl orange or phenolphthalein. It also differs from phosphoric acid in the uniformity with which its acid alkali salts precipitate acid salts, and its neutral alkali salts give neutral salts. No exception to this was observed. Soluble acid phosphates, as is well known, give, with silver and many other metals, precipitates of neutral salt.

The investigation will be continued in the directions indicated. The above data were worked out, for the most part, in the chemical laboratory of the United States Geological Survey, in Washington, and I am indebted to the director, Major Powell, and to Professor F. W. Clarke, for the opportunity of so doing.

CHICAGO, *Jan.*, 1893.

DERIVATIVES OF NITROGEN HALOGEN COMPOUNDS.

First Paper.

By Felix Lengfeld and Julius Stieglitz.

An article by Seliwanow in Berichte **25**, p. 3617, on "Mixed Anhydrides of Hypochlorous and Analogous Acids," leads us to publish this preliminary report. Our work was undertaken for the purpose of obtaining substituted hydroxylamines and hydrothiamines (NH_2SH) by the action of the compounds ROMe and RSMe on HalNR, and of ROHal and RSHal on MeNR. We propose continuing our work in this direction, and shall, of course, avoid as far as possible questions dealing with the derivation of the halogen amides and amines from hypochlorous and analogous acids, as outlined in Seliwanow's paper.

As the substituted succinimides $C_2H_4(CO)_2NR$ are readily decomposed into succinic acid and amines, it is probable that compounds $C_2H_4(CO)_2NOR$ will yield hydroxylamines without difficulty ; and this, together with the fact that succinimide is easily obtained, led us to begin our investigation with the halogen derivatives of succinimide. We found that succinimidebromide (bromylsuccinimide, if Seliwanow's nomenclature is adopted) can be prepared in quantity with little trouble. This was acted on with sodium alcoholates in order to obtain oximethers of succinic acid according to the equation

$$\begin{matrix} CH_2-CO \\ | \qquad\qquad >NBr+NaOR= \\ CH_2-CO \end{matrix} \quad \begin{matrix} CH_2-CO \\ | \qquad\qquad >NOR+NaBr. \\ CH_2-CO \end{matrix}$$
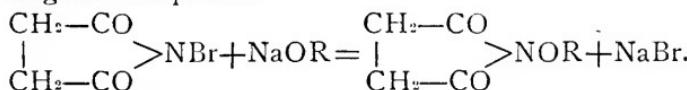
The reaction, however, is not so simple.

<p align="center">*Succinimidebromide,*</p>

$$\begin{matrix} CH_2-CO \\ | \qquad\qquad >NBr \text{ or} \\ CH_2-CO \end{matrix} \quad \begin{matrix} CH_2-C-O-Br \\ | \qquad\qquad >N \\ CH_2-C-O \end{matrix}$$
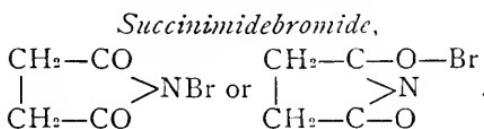
20 grams of succinimide are dissolved in a solution of 8 grams sodic hydrate in 50 cc. water, placed in cracked ice, and 32 grams bromine slowly added. The first few drops of bromine produce a white crystalline precipitate which, on further addition, increases

so that the mass becomes thick and pasty. It is rapidly filtered, washed with a little ice-water and brought on clay plates. Any excess of bromine volatilises, and a microcrystalline, almost colorless powder, sufficiently pure for most purposes, remains. The yield is from 90 to 95 per cent. of the theoretical. A slight variation in the details, such as the use of potassic instead of sodic hydrate, or the addition of the alkali to a mixture of bromine and succinimide, does not affect the result. A perfectly white compound may be obtained by replacing one-fourth of the water by ethyl alcohol. The reaction is evidently as follows:

$$C_4H_5NO_2 + NaOH + Br_2 = \begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix}\!\!>\!\!NBr \text{ or}$$

$$\left(\begin{matrix} CH_2-C-O-Br \\ | \qquad\quad >N \\ CH_2-C-O \end{matrix} \right) + NaBr + H_2O.$$
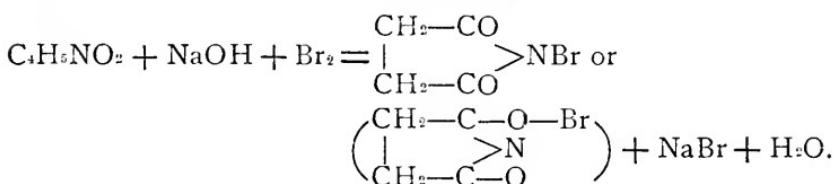
For analysis, the compound was washed repeatedly with cold water and dried first on clay plates, then in a vacuum over sulphuric acid, and finally in an air-bath at 80° for one hour. The following results were obtained:

I.   0.2285 gram substance gave 0.225 gram CO_2 and 0.0528 gram H_2O.

II.   0.2261 gram substance gave 14.7 cc. moist N at 4.5° and 747 mm.

	Calculated for $C_4H_4NO_2Br$.	Found. I.	II.
C	26.97	26.84	...
H	2.25	2.57	...
N	7.87	...	7.85

Succinimidebromide melts at 172.5° when slowly heated, and at 177.5°–178.5° when rapidly heated. Pure, it melts with but slight decomposition, and recrystallises on cooling. When it contains even a trace of impurity, its fusion is attended with decomposition and evolution of gas. From hot benzene (in which it is sparingly soluble) it crystallises in short tetragonal prisms with pyramidal terminations. It has, in general, the same properties as acetbromamide.[1] Acids instantly liberate bromine, regenerating succinimide; with ammonia it gives nitrogen; with aniline it reacts with explosive violence, and with sodium phenolate it

[1] Hofmann, *Ber.* **15**, 411.

forms tribromphenol.   Water decomposes it slowly, the solution
bleaching. Pure and dry, it is stable and may be kept indefinitely.
It is evidently analogous to succinimideiodide prepared by
Bunge[1] by the action of iodine on silver succinimide in anhydrous
solution, and to succinimidechloride obtained by Bender[2] from
succinimide, bleaching powder and hydrochloric acid.   It would
seem, however, to be somewhat more reactive, as all attempts to
replace the halogen in the chlor- and iodo-compounds have failed,[3]
and the following reactions show that the bromine is replaceable.

Action of Succinimidebromide on Sodium Methylate in Dilute Solution.

The action of sodium methylate in methyl alcohol on succinimide-
bromide varies with the concentration.   1 gram sodium (1 atom) is
dissolved in 40 grams pure methyl alcohol, the solution cooled,
8 grams succinimidebromide (1 molecule) added, and the whole
boiled on a water-bath with inverted condenser forty minutes.   It
is now alkaline, but gives no bromine on adding hydrochloric acid.
It is almost neutralised with hydrochloric acid, and then acetic
acid in slight excess is added.   The methyl alcohol is removed
by distillation, the residue repeatedly extracted with chloroform,
and the chloroform, after washing first with a very dilute sodic
hydrate solution, then with acidulated and pure water, and drying,
distilled off.   There remains a straw-colored oil which solidifies
in a freezing mixture, but melts again at the ordinary temperature
of the laboratory.   It is a mixture of at least two compounds, one
of which is readily, the other difficultly soluble in ether.   The
difficultly soluble compound is present in but small quantity and
is identical with the substance described on p. 219.   The ethereal
solution on evaporation leaves an oil which may be distilled in a
vacuum.   The main portion goes over between 145.5° and 146.5°
(thermometer in the vapor) at 20 mm. pressure.   It is a colorless
oil which soon solidifies to a crystalline mass, especially on cooling
or stirring.   It now remains solid at the temperature of the labor-
atory.   It melts at 33.5°, is odorless, and easily soluble in water
and the organic solvents, with the exception of ligroin.   The yield
of crude oil is about 55 per cent. of the theoretical, of pure sub-
stance about 40 per cent.   We have not yet further investigated

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[1] Annalen, Sup. **2**, 119.   [2] Berichte **19**, 2273.
[3] Bunge, loc. cit.; Bender, loc. cit. p. 2274 ; Seliwanow, loc. cit., 3620, etc.

the residue left on distilling the crude oil. The compound melting at 33.5° was powdered, put on a clay plate and left in a vacuum over sulphuric acid for forty-eight hours. Analysis then gave the following results:

I. 0.2194 gram substance gave 0.3576 gram CO_2 and 0.1354 gram H_2O.

II. 0.2058 gram substance gave 0.330 gram CO_2 and 0.1281 gram H_2O.

III. 0.2328 gram substance gave 0.3790 gram CO_2 and 0.148 gram H_2O.

IV. 0.210 gram substance gave 15.4 cc. moist nitrogen at 11° and 750.3 mm.

	Calculated for $C_6H_{11}O_4N$.	I.	II.	III.	IV.
				Found.	
C	44.72	44.45	44.13	44.40	...
H	6.83	6.86	6.92	7.06	...
N	8.70	...	...	...	8.63

A determination of the molecular weight by the cryoscopic method, water as solvent, gave the following:

Weight of water used, 15.17 grams.

I. 0.352 gram substance depressed the melting-point 0.279°.

II. 0.643 gram substance depressed the melting-point 0.48°.

III. 0.9585 gram substance depressed the melting-point 0.69°.

Molecular weight calculated for $C_6H_{11}O_4N$.	I.	II.	III.
		Found.	
161	158	167.8	174

We have evidently a compound of the formula $C_6H_{11}O_4N$ formed by the following reaction:

$$C_2H_4(CO)_2NBr + NaOCH_3 + HOCH_3 = C_6H_{11}NO_4 + NaBr.$$
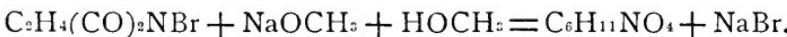
The method of formation suggests the constitution

$$\begin{array}{l} CH_2{-}COOCH_3 \\ | \\ CH_2{-}CONH.OCH_3 \end{array}$$
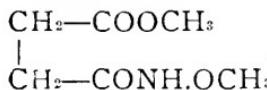
Such a substance should give substituted hydroxylamines, and like the oxime ethers $C{=}O$ $\begin{array}{c} NHR' \\ \diagdown O_2R \end{array}$ readily yield an acid by the substitution of hydrogen for carboxylic methyl. On shaking with milk of lime,[1] the calcium salt of an acid is indeed formed. The alkaline

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[1] Wallach: Annalen **184**, 58.

solution is washed with ether, and after acidifying with hydrochloric acid, repeatedly extracted with ether or chloroform. On distilling the solvent, a colorless oil which soon solidifies remains. It may be purified by dissolving in a little chloroform and precipitating with ligroin (boiling-point 40°–60°). For analysis it was prepared in this way and dried on clay plates in a vacuum over sulphuric acid for 48 hours. The following results were obtained:

I. 0.2035 gram substance gave 0.300 gram CO_2 and 0.115 gram H_2O.

II. 0.2539 gram substance gave 21.0 cc. moist nitrogen at 19.5° and 747.7 mm.

	Calculated for $C_5H_9NO_4$.	Found. I.	II.
C	40.81	40.21	...
H	6.12	6.28	...
N	9.52	...	9.54

Analysis agrees with a compound, $CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NHOCH_3.$—The $CH_2-COOH.$

substance has acid reaction, taste and properties. It melts at 77°–77.5° and is easily soluble in water and the organic solvents, excepting ligroin. From ether it crystallises in fan-like acicular aggregates. It will be carefully studied. From it and the substance melting at 33.5°, probably its methyl ether, we are now trying to obtain α-methylhydroxylamine.

Action of Sodiummethylate in Concentrated Solution on Succinimidebromide.

1 gram of sodium (1 atom) was dissolved in 8 grams of pure methyl alcohol, and to the cold solution 8 grams (1 molecule) succinimidebromide added. An energetic reaction immediately takes place, the mixture becoming so warm that the methyl alcohol boils. The reaction is completed by heating 10 to 15 minutes on a water-bath. After cooling the mixture, it is nearly neutralised with hydrochloric acid and then rendered slightly acid with acetic acid and evaporated. The residue is treated exactly as described above (page 217). The oil remaining after driving off the chloroform readily deposits a mass of crystals when treated, in a freezing mixture, with ether. The crystals may be

separated by filtration from the ethereal solution and dried on clay plates. A second crop of these crystals having been obtained from the mother-liquor by evaporating the solvent, cooling and adding very little ether, the ethereal washings now leave on evaporation only a small amount of an oil, which in a freezing mixture gives white crystals, melting at 33.5°, and identical with the compound $C_6H_{11}NO_4$ described above. The chief product of the reaction, already quite pure, was purified for analysis by repeatedly dissolving in very little chloroform, cooling in an ice-mixture and precipitating with ether. The compound thus obtained melts at 65.5°, is readily soluble in water, alcohol and chloroform, difficultly soluble in ether, and crystallises from ether in stellar acicular aggregates. For analysis the substance was dried at 100°.

I. 0.2346 gram gave 0.1307 gram H_2O and 0.3942 gram CO_2.

II. 0.1461 gram gave 13.7 cc. moist nitrogen at 9° and 747 mm.

III. 0.2097 gram gave 0.118 gram H_2O and 0.3513 gram CO_2.

IV. 0.229 gram gave 0.1312 gram H_2O and 0.3883 gram CO_2.

V. 0.1575 gram gave 15.1 cc. moist N at 17.5° and 751 mm.

	Calculated for $C_{10}H_{16}O_6N_2$.	I.	II.	Found. III.	IV.	V.
C	46.15	45.80	...	45.7	46.24	...
H	6.15	6.18	...	6.25	6.37	...
N	10.77	...	11.11	...	...	11.15
O	36.93	...	...	...	...	...

A cryoscopic determination of the molecular weight, using benzene as solvent, gave abnormally high values (400 and over) which varied with the concentration. With water the values proved normal.

Weight of water used, 16.87 grams.

I. 0.0903 gram substance gave a mp. depression of 0.042°.

II. 0.3488 gram gave 0.1475°.

III. 0.5768 gram gave 0.2465°.

Calculated for $C_5H_7NO_3$.	Calculated for $C_{10}H_{16}O_6N_2$.	I.	Found. II.	III.
129	260	242.1	266.3	263.5

The average yield obtained from 40 grams succinimidebromide was 30 grams crude $C_{10}H_{16}O_6N_2$ and only very little $C_6H_{11}NO_4$. The result of the reaction is therefore, in so far as the relative quantities of the products are concerned, the reverse of that when working with dilute solution. In working in concentrated solu-

tion, *succinimide* is always formed ; being difficultly soluble in chloroform, it crystallises first, when the chloroform extraction of the reaction residue has not been washed with dilute sodic hydrate. The succinimide was identified by its melting-point (124°) and its general behavior.   It is no doubt formed by the reducing action of the methyl alcohol on the imidebromide, the odor of formaldehyde being quite noticeable during the reaction.   It is very probable that the formation of the compound $C_{10}H_{16}N_2O_6$ depends on this previous formation of succinimide, according to the following equation :

$$C_2H_4C_2O_2NBr + C_2H_4C_2O_2NaN + 2CH_3OH = NaBr + C_{10}H_{16}O_6N_2.$$
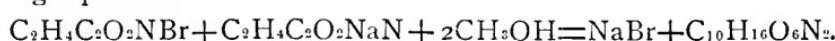
If this view is correct, the principal reaction is essentially of the same nature in dilute and in concentrated solution,—succinimide-bromide reacting in the first case with *sodium methylate* and methyl alcohol, in the second case with *sodium succinimide* and methyl alcohol.   The decomposition of $C_{10}H_{16}N_2O_6$ tends to confirm this view.   On being treated with concentrated hydrochloric acid in the cold (2 days) or at 100° (at once), it yields about equal quantities of *succinic acid* (identified by its melting-point, 180°, and by qualitative tests) and of a new compound, $C_4H_6O_2N_2$. This substance is very difficultly soluble in hot absolute alcohol, and so its separation from the succinic acid, which is fairly soluble, can be readily effected.   The compound was recrystallised from boiling 50 per cent. alcohol, being deposited, on cooling, in small, colorless, irregular plates.   Analyses of the compound as dried at 100° gave:

I. 0.2272 gram substance gave 46.15 cc. moist N at 4.5° and 744 mm.

II. 0.232 gram gave 0.1147 gram H_2O and 0.3602 gram CO_2.

	Calculated for $C_4H_6O_2N_2$.	I.	II.
		Found.	
C	42.10	...	42.34
H	5.26	...	5.49
N	24.56	24.42	...
O	28.08	...	...

A determination of the molecular weight was made by the ebulliscopic method, the substance being but slightly soluble in cold water.

0.4813 gram substance dissolved in 23 grams H_2O raised the boiling-point 0.094°.

Calculated for $C_4H_6O_2N_2$.	Found.
114	115.7

The substance melts with some decomposition at 272°, is somewhat soluble in cold water, more readily in hot water, very little in strong alcohol, and scarcely in chloroform, ether, etc. It has a neutral reaction, and is remarkably stable, remaining unchanged when heated with conc. hydrochloric acid to 150° in a sealed tube. It is obtained from $C_{10}H_{16}N_2O_6$ by a second simple reaction, *viz.* by boiling with 1 molecule of sodium methylate in methyl alcohol. On cooling, the substance $C_4H_6N_2O_2$ crystallises out, and the filtrate yields an oil having the odor of methyl succinate.

The decomposition of $C_{10}H_{16}N_2O_6$ by hydrochloric acid may be expressed in:

$$C_{10}H_{16}N_2O_6 + 2H_2O = C_4H_6O_2N_2 + C_2H_4(COOH)_2 + 2CH_2OH.$$

The formation of $C_{10}H_{16}N_2O_6$ from two molecules of a *mononitrogen* derivative of succinic acid, and its decomposition into succinic acid and a *dinitrogen* compound, $C_4H_6O_2N_2$, indicate that the two residues in the larger molecule are linked together by one or both the nitrogen atoms and that we therefore very probably have derivatives of hydroxylamine or of hydrazine.

Further investigations are being made to prove the absolute constitution of all of these compounds, and we hope that the reactions indicated in the opening paragraph may be left to us for full investigation.

CHICAGO, *February 7*, 1893.

NOTES.

Obituary.

Frederick Augustus Genth, for many years Professor of Chemistry and Mineralogy in the University of Pennsylvania, died in Philadelphia, February 2, 1893, in the seventy-third year of his age.

He was a native of Hesse-Cassel. After studying at Heidelberg and in Liebig's laboratory at Giessen, he received his

doctor's degree at Marburg. Here, too, he served as assistant to Professor Bunsen until he came to the United States.

Professor Genth is chiefly known as a mineralogist, his work, so far as published, having been, with a few important exceptions, confined to that branch of natural science. As official mineralogist he contributed several important monographs upon the mineralogy of Pennsylvania, North Carolina, etc. His principal work on purely chemical lines was the discovery and investigation of the cobalt-ammonium compounds.

He was an exceedingly active, enthusiastic investigator from his student-days to within a short time of his death. His zeal in the encouragement of scientific research entitles him to the grateful remembrance of American mineralogists and chemists.

W. W. R.

The Electrolytic Dissociation of Acids in Solution.

In a paper entitled " Ueber die Messung kleiner Dissociationsgrade," J. E. Trevor [1] gives the results of his studies of the inverting action of weak acids and acid salts on sugar solutions at 100°. The method gave accurate results, a preliminary experiment having shown that if no hydrogen ions be present, a sugar solution may be kept 80 minutes at 100° without being perceptibly inverted. To obtain comparable results it was found necessary always to use solutions of the same strength, as the sugar concentration has an effect as yet unexplained on the dissociation.

The inverting velocity of a given concentration of hydrogen ions is more than 400 times as great at 100° as at 25°. If $c =$ the inversion-velocity of any acid, we shall have for its temperature-coefficient $I = \delta \log c / \delta T$. The author found that the values for I were practically identical for a large series of acids, including those of all possible types. As he had already shown that for dilutions greater than 200, hydrochloric acid may be considered as completely dissociated both at 25° and at 100°, it follows that, if $I =$ a constant, the dissociation of the other acids must be the same at 25° as at 100°; in other words, that the dissociation is a function of the volume only and not of the temperature. If this be true, the increase of the conductivity with the temperature is not to be accounted for by an increase in the dissociation, and the conclusions of Arrhenius [2] refer to some other property of electrolytes. In the equation of van't Hoff, $\delta \log c / \delta T = q / R T^2$, if $\delta \log c / \delta T = 0$, then $q = 0$, and what is known as the electrolytic heat of dissociation is due to another cause.

The measurements on the hydrogen dissociation of acid salts is interesting as being the first contribution to our knowledge of this subject, and it is astonishing with what accuracy these slight dissociations can be determined by this method. Of the acid sodium

[1] Ztsch. phys. Chem. **10**, 231.   [2] *Ibid.* **4**, 96.

salts of the dibasic organic acids the fumarate is the only one where the hydrogen ion is 1 per cent. dissociated at a dilution of 100 : 1. From the measurements no satisfactory conclusions in regard to chemical constitution could be drawn, and the predictions of Ostwald [1] cannot be said to have been entirely confirmed.

W. D. B.

Errata.

Page 22, line 4 (from top), for " stereo-isomeric " read *identical*.

Page 22, line 22 (from bottom), for " *d*. gluconic acid " read *d. gulonic acid.*

Page 26, line 7 (from top), for " potassium " read *potash*.

Page 28, line 22 (from top), for " when several cc. were used " read *within a few cc. of the distillate.*

Page 28, line 3 (from bottom), for " 40 cc. of the clear solution (see above) were treated successively with lead acetate and with sodium sulphate, and after being subjected to the process of inversion and neutralised, were filled up to 50 cc." read *40 cc. of the clear solution (see above) which had been previously treated successively with lead vinegar and with sodium sulphate, were subjected to the process of inversion, neutralised and filled up to 50 cc.*

Page 30, line 27 (from top), for " of the furfurol " read " *of furfurol.*"

Page 30, line 9 (from bottom), for " 0.45 " read 0.045.

Page 30, line 8 (from bottom), for " 0.45 " read 0.045.

Page 37, line 15 (from top), for " pentoses " read *hexoses*.

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[1] Ber. d. k. sächs. Ges. der Wiss., 1891, p. 233; Ztsch. phys. Chem. **9,** 553.

AMERICAN

CHEMICAL JOURNAL.

THE HYDRATES OF MANGANOUS SULPHATE.

By C. E. Linebarger.

Water has the faculty of entering into combination with certain chemical compounds, forming the so-called " hydrates." For convenience of reference these hydrates may be divided into three classes, although the lines of division are somewhat dim and arbitrary. Still, a classification may aid us in concentrating our attention and in obtaining precise ideas, thus enabling us to get a better insight into the nature of such compounds.

The first class embraces the hydrates of colloid or non-crystalline substances. When such compounds as silica, the hydroxides of iron, aluminium, etc., pass out of solution, solid non-crystalline masses are formed, containing variable quantities of water. If such hydrates be dried at definite temperatures and pressures, they sometimes have a fixed composition in stoichiometrical ratios. Generally, however, the water contained in them passes off continuously with rise of temperature. Our knowledge of the nature of colloids[1] is so vague that it would be premature to present any general considerations relative to their hydrates. Indeed, the colloid state seems often to depend upon the presence of " hydrate-water." A very interesting and fruitful field of investigation is to be found here, the working of which is very desirable.

The second class comprises the hydrates of the acids, bases, alcohols and the like. Their hydrate-water seems to enter into the intimate constitution of the molecule. In these compounds

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[1] See my paper " On the Nature of Colloid Solutions," Am. J. Sci. **43**, 218.

there is generally no outward sign of their containing water, which is bound so firmly that often it cannot be removed without the entire character of the substance being changed. In this class, the "hydrate-water" may not be separated from the acid, base, or alcohol, as the case may be, by the act of solution, and we may perhaps in some cases speak of the hydrates existing as such in solution.

The third class of hydrates takes in those of the salts. Although salts made up of univalent bases and acid radicles do not, with a few exceptions, form crystalline compounds with water, this property is enjoyed to a considerable degree by salts composed of multivalent bases and acid radicles. Double salts also, even if consisting of salts which do not themselves form hydrates, almost invariably crystallize with water.

The above classification is indeed imperfect, yet it permits us to make certain distinctions that are likely to be overlooked. We have no right to apply hypotheses based upon phenomena observed in one class to phenomena observed in another. The existence of hydrates as such in liquid solution is a debated question. Now, nearly all the conclusions favoring the assumption of hydrates in solution are drawn from facts gleaned in the study of the behavior of solutions of hydrates of the second class. Even if hydrates of sulphuric and nitric acids, etc., be shown to exist in solution, it cannot at once be affirmed that hydrates of the third class are also capable of existence in solution. On the other hand, even if the physical constants of solutions of salts are identical, no matter what the hydrate from which the solution is prepared, the conclusion that hydrates of acids, etc., cannot exist in solution does not necessarily follow. Each class of hydrates must be considered by itself; conclusions in regard to one class cannot be extended to another.

The existence of hydrates of the first class in solution— a possibility which seems not to have received much attention—is rendered probable from the fact that most of the dehydrated colloids are quite indifferent towards water; once deprived of water, they become insoluble. As stated above, the colloid state is perhaps dependent upon the "hydrate-water."

The water of crystallization plays much the same rôle as the water of solution. If it be admitted that certain salts be decomposed into their ions when dissolved in water, the conclusion

necessarily follows that such a decomposition is effected by the water of crystallization.[1]

As such an intimate connection prevails between "crystallo-hydrates" and their saturated solutions, a thorough study of the latter should give important information with regard to the former. Much work has been done upon the subject of solubility, but most of it does not take into consideration the principle that solutions are saturated only with respect to a distinct nucleus. Saturated solutions of hydrates are cases of dynamic equilibrium between a definite hydrate and the solution. As soon as the hydrate changes, the solubility changes also. This principle—first formulated by Ostwald (1885), although Demarçay,[2] in a study of the sulphates of thorium, had shown its necessity—is of fundamental importance. The maximum amount of a salt that can enter into solution depends principally upon the temperature and its state of hydration. The solubilities of the various hydrates of a salt are in general different, and at the temperature where one hydrate changes into another there is a break in the continuity of the curve representing the solubility. The determination of the solubility of salt hydrates accordingly affords a valuable means of ascertaining what are their limits of stability. Determinations of the solubilities of all the hydrates of a salt have been made in but few instances.[3] Although not much that is novel can be expected from the study of further examples, it is nevertheless important to illustrate the principles of the states of equilibrium of heterogeneous systems, of which solutions of hydrates are cases, by as great a variety of examples as possible. The present paper accordingly treats of the hydrates of manganous sulphate throughout their entire range of solubility, giving a general survey of their behavior and limits of stability.

A common way of preparing hydrates consists in driving off water (by heat, exposure in a vacuum to dehydrating substances, etc.) from a higher hydrate, until a compound is obtained in which the quantities of salt and water are in simple stoichiometrical ratio. It is then assumed that the desired hydrate is formed. In reality, however, there is no ground for any such assumption, unless the

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[1] See my paper "On the Dissociation of Salts into their Ions by Water of Crystallization," This Journal **14**, 604.

[2] Compt. rend. **96**, 1859 [1883].

[3] Most of these have been done by Bakhuis Roozeboom, and are published in the Zeitschrift für physikalische Chemie.

hydrate has been shown actually to crystallize from its solution ; and even then we cannot assume that hydrates formed according to such different methods will have the same properties, for isomeric hydrates are capable of existence. The assumed hydrate may be merely a mixture of the higher hydrate and anhydrous salt or lower hydrate. It is quite probable that a mixture of several hydrates may be formed in such proportions that its composition corresponds to that of a definite hydrate. It is easy to obtain intermediate mixtures containing any desired fraction of a molecule of water, and we have as much right to suppose that we then have a definite hydrate as when we hit upon an integral number of molecules. A true criterion of a fixed hydrate is its capability of crystallizing from solution spontaneously. In the study of the hydrates of manganous sulphate, my first object was to prepare hydrates answering to the above criterion. This was done in two ways : 1. Solutions of the salt were allowed to deposit crystals at different constant temperatures, the amount of " hydrate-water " being a function of temperature, the higher the latter, the less the former. 2. Liquids which have great attraction for water and no chemical action upon manganous sulphate, such as sulphuric acid and alcohol, were added to a solution of the salt, the amount of water of crystallization being thus diminished. Below, under each hydrate are given the methods of preparing it.

A definite hydrate once obtained, the next thing was to determine its solubility ; the methods employed and apparatus used are described below under the head of " Determinations of Solubilities."

The solubilities of the hydrates being obtained and curves representing them constructed (Fig. 2), we can compare and discuss them (page 240) and treat of any special points that suggest themselves (page 246).

Determination of Solubilities.

The accuracy of a determination of solubility depends largely upon the constancy of the temperature at which a determination is being made. For temperatures between 25° and 60° I made use of a so-called " Ostwald's thermostat." Its temperature during an experiment did not vary more than 0.1°, and not more than 0.2° to 0.3° from day to day. In order to reduce the influence of a change of temperature in the laboratory upon the

temperature of the thermostat, the thermo-regulator was almost wholly immersed in the water contained in the thermostat. The windmill which drove the paddles was made entirely of wood. Such a one is easily constructed out of thin pine paddles set in a hub, and is so stiff and can be so delicately poised that it requires but a very weak current of air to run it. For temperatures between 60° and 180° a large bath of sulphuric acid or of glycerine was employed; between 25° and 0° about three gallons of water were heated or cooled to the desired temperature and used as a bath; below 0°, solutions of common salt were used. By stirring constantly and adding hot water, ice or a mixture of ice and snow, as might be required, it was possible to keep the temperature from varying more than 0.5°.

Equilibrium between the hydrate and its solution was attained in four ways, each being employed throughout a certain range of temperature.

For temperatures below 10°, the hydrate, broken up into small fragments, together with a solution containing about 50 parts of salt to 100 parts of water, was introduced into a small flask, which was set in a bath at the desired temperature. The contents of the flask were well shaken every 15-20 minutes during at least three hours. A sample of the solution was then drawn off by means of a pipette provided with a filtering arrangement, about 10 cc. being taken. This was run into a little glass boat, such as described by Trevor,[1] and the water drawn off. To expel the last traces of water, the salt was heated in the boat to 160°-170° in an air-bath.

The apparatus sketched in Fig. 1 was used in the determination of solubilities between 10° and 60°. AB is a glass tube having a length of 5 inches and an internal diameter of about 0.8 inch. At its bottom the tube e is melted in, which establishes communication with the tube C. A bit of rubber tubing is slipped over one end of e at t, into which passes easily but tightly the glass rod pa. In making a determination, a little wad of cotton-wool is placed in the projecting part of the bit of rubber tubing, and the rod pq pressed down upon it, the cotton acting as a filter. Coarsely-powdered hydrate is now put into the tube AB, and enough of a solution of manganous sulphate of about 50 per cent. to fill the tube a little more than half. The stirrer rs, a piece of

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[1] Ztschr. phys. Chem. **7**, 468 (1891).

stout platinum wire, is put in position and the cork D inserted.
After the tube C has been attached, the apparatus is put in the
thermostat and its contents stirred
frequently. After three or four
hours, the solution is allowed to
settle and the rod pa raised. By
means of a suction-pump connect-
ed to the tube xy, the clear solu-
tion is drawn over into C. A por-
tion of this is poured into a glass
boat and the water driven off as
described above.
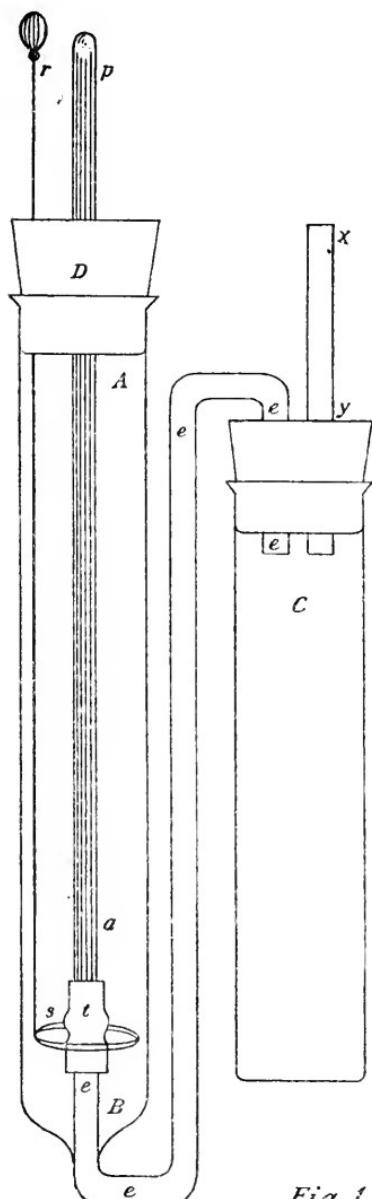
It is impossible to employ either
of the above methods in deter-
mining the solubility of the mono-
hydrate, the only hydrate stable
above 60°. Therefore the follow-
ing procedure had to be adopted
for temperatures up to 100°. A
weighed quantity of a solution of
manganous sulphate of known
concentration was evaporated on
the water-bath until the mono-
hydrate just began to separate
out. The flask was then removed
from the bath, and, after its neck
was carefully wiped dry on the
inside, weighed. At the tempera-
ture of the laboratory, the mono-
hydrate soon entered into solu-
tion. The clear solution was now
heated to 100°, this time with the
flask tightly corked. Invariably
the separation of the hydrate en-
sued so soon as the solution at-
tained the temperature of the
bath. A slight calculation gives
the solubility of the hydrate at

Fig. 1

100°. For temperatures lower than 100° more of the water was
driven off, the solution allowed to stand until the precipitated

hydrate had again dissolved, and the clear solution heated in a bath of glycerine, a little mono-hydrate being thrown in from time to time to avoid supersaturation. The temperature at which the hydrate appeared was, for a definite concentration, a fixed one.

The solubility above 100° was determined by heating solutions of known concentration in sealed hard-glass tubes until a separation of solid took place.

Modes of Expressing Solubilities.

Although the principal phenomena of solubility had been known from earliest times, no really scientific investigation was carried out before the year 1819, when Gay Lussac published a paper on the subject,[1] in which he gave his results a graphical representation. The curves were so constructed that temperatures were laid off along the axis of abscissæ, and the number of parts of substance dissolved in 100 parts of water was measured on the axis of ordinates. Gay Lussac was probably led to adopt this method of representation in order to shape his results to practical ends. The example thus set has been followed by almost all who have occupied themselves with the question of solubility. But with this mode of representation the determinations in aqueous solution are confined within rather narrow limits, *viz.*, 0° and 100°. But below 0° and above 100°, substances can still be held in solution. Hence a need arises for another mode of representation not subject to these limitations. Étard seems to have been the first to propose a new mode of graphical representation.[2] Instead of taking as ordinate the amount of substance that 100 parts of water can dissolve, he takes the quantity of substance contained in 100 parts of the saturated solution. Thus, one of the values is a function of the other ; when the quantity of substance increases, the quantity of solvent decreases, and all the results are comparable, being comprised between 0 per cent. and 100 per cent. of dissolved substance. The results when plotted give straight lines, and if an interpolation formula be made it takes the form

$$y''_{t_o} = a + bt_o,$$

where y''_{t_o} indicates the solubility between t_o and t', a the ordinate of solubility at the origin, and b the coefficient of solubility for every degree.

[1] Ann. chim. phys. [2] **11**, 296.   [2] Compt. rend. **98**, 993; 1276; 1432; **104**, 1614.

It must be said that this "straightness" of the curves is in a measure due to the choice of the values of ordinates and abscissæ. The curves never have any considerable inclination towards the axis of ordinates, and curved lines are easily smoothed down into approximately straight lines. The curve is a branch of a hyperbola, which is practically straight for moderate concentrations. Still this mode of representation is valuable, inasmuch as it shows clearly how solution passes into fusion.

A more rational mode of expressing solubilities is by the use of molecular numbers, for these only are chemically comparable. There are two ways that may be employed : (1) The ratio of the number of molecules of dissolved substance to any number (generally 100) molecules of the solvent ; (2) the ratio of the number of molecules of dissolved substance to any arbitrary (usually 100) number of molecules of the solution. The second of these two methods seems to be peculiarly adapted to the representation of the relations of the physical constants of solutions of various salts.

As my object in determining the solubilities of the hydrates of manganous sulphate was simply to get information as to their limits of stability, I have employed the mode proposed by Gay Lussac, which shows clearly the changes undergone by the different hydrates at different temperatures.

Hepta-hydrate : $MnSO_4.7H_2O$.

If a solution containing from 60 to 70 parts manganous sulphate to 100 parts water be exposed to a temperature below 5°, a mass of pinkish monoclinic crystals soon separates out, which possess the formula $MnSO_4.7H_2O$. The appearance and properties of the hepta-hydrate have been described by Brandes[1] and Carnot.[2] It has been found in "crystalline masses with fibrous structure" in Utah, being known as the mineral Mallardite. It loses some of its water of crystallization at rather low temperatures ; thus Brandes states that it became soft at 12°, and a viscous liquid at 18°, while at 24° it turned into a white, porridge-like mass. This behavior is undoubtedly due to its changing into hydrates containing less water of crystallization.

Two series of determinations of its solubility were made, one from —10° to 7°, the other from —10° to 58°. In the second series the hydrate was heated with its solution in a flask slowly and con-

[1] Ann. der Phys. Pogg. **20,** 578.   [2] Bull. Soc. Min. **2,** 117.

tinuously, samples of the solution being removed after every five degrees rise in temperature. The results are given in Tables I and II; those of I being represented graphically in Fig. 2 (curve 7, 7).
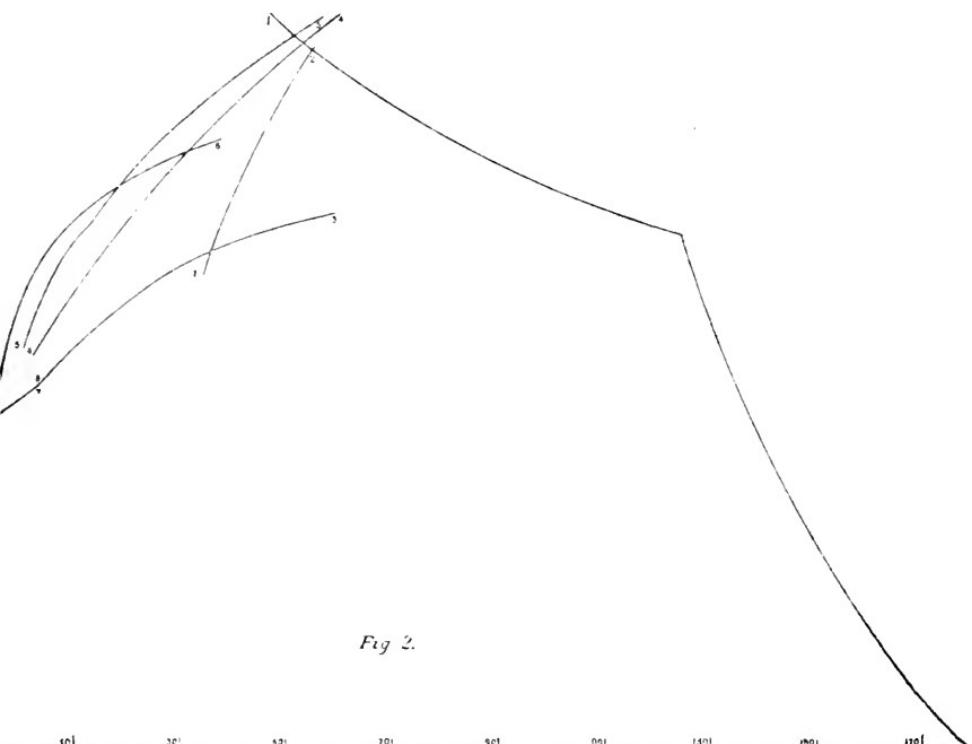
Fig 2.

TABLE I.

Solubility of $MnSO_4.7H_2O.$ — *Series* 1.

Temperatures,	—10°	—8°	—5°	0°	5°	7°
Parts $MnSO_4$ to 100 parts H_2O,	50.11	50.93	51.53	53.61	54.83	56.62

TABLE II.

Solubility of $MnSO_4.7H_2O.$ — *Series* 2.

Temperatures,	—10°	—5°	0°	5°	10°	15°
Parts $MnSO_4$ to 100 parts H_2O,	50.24	51.71	53.46	54.73	59.91	64.34

Temperatures,	20°	25°	35°	45°	54°	58°
Parts $MnSO_4$ to 100 parts H_2O,	66.61	67.14	68.51	70.33	73.06	72.94

Hexa-hydrate : $MnSO_4.6H_2O$.

It was remarked by Brandes[1] that the hepta-hydrate, if allowed to stand at temperatures in the neighborhood of 10°, gradually loses one molecule of water, being converted into the hexa-hydrate. I have found that a warm solution of manganous sulphate containing about 80 per cent. of the anhydrous salt, when cooled to 2°–5°, deposits small hexagonal plates, the composition of which corresponds to the formula $MnSO_4.6H_2O$. By sowing some of the crystals thus obtained in a solution maintained at 0°, large, well-formed crystals separate out.

The solubilities of the hexa-hydrate are given in Table III, and graphically in Fig. 2 (curve 6, 6).

TABLE III.

Solubility of $MnSO_4.6H_2O$.

Temperatures,	−4°	0°	3°	5°	9°	15°
Parts $MnSO_4$ to 100 parts H_2O,	55.87	64.21	66.87	67.49	70.88	72.45
Temperatures,	20°	25°	30°	34°	35°	38°
Parts $MnSO_4$ to 100 parts H_2O,	74.35	75.38	76.24	77.02	77.23	78.41

Penta-hydrate : $MnSO_4.5H_2O$.

Solutions of manganous sulphate evaporated at 10°–15° deposit triclinic crystals of the penta-hydrated salt. It was obtained by Brandes by the abstraction of two molecules of water from the hepta-hydrate by the action of absolute alcohol.

In Table IV are given the results of the determinations of the solubility of the penta-hydrate, which are represented graphically in Fig. 2 (curve 5, 5).

[1] *Loc. cit.*

TABLE IV.

Solubility of $MnSO_4.5H_2O$.

Temperatures,	0°	2.5°	4°	7°	10°	15°
Parts MnSO₄ to						
100 parts H₂O,	58.05	62.41	64.22	66.83	68.05	72.33
Temperatures,	20°	25°	30°	32°	34°	37°
Parts MnSO₄ to						
100 parts H₂O,	75.16	78.63	79.16	80.38	82.04	83.91
Temperatures,	40°	42°	45°	47.7°	53°	54°
Parts MnSO₄ to						
100 parts H₂O,	84.63	85.27	86.16	86.95	88.89	89.08

Tetra-hydrate: $MnSO_4.4H_2O$.

It is in the form of the tetra-hydrate that manganous sulphate comes upon the market. This is due to the fact that this hydrate separates out of its solution at ordinary temperature (18°–20°). It was obtained by Brandes[1] by the decomposition of higher hydrates by the action of alcohol and heat.

An excellent method for obtaining it rapidly is the following: A strong solution of manganous sulphate is shaken up well with half its volume of strong alcohol. On standing, the solution promptly separates into two layers, in the lower of which crystals soon appear. After a few hours an abundant crop of crystals is obtained which have the same solubility as those crystallized from aqueous solution alone.

The results of the determinations of its solubility are given in Table V, and represented graphically in Fig. 2 (curve 4, 4).

TABLE V.

Solubility of $MnSO_4.4H_2O$.

Temperatures,	2.2°	7.3°	11°	15°	20°	25°
Parts MnSO₄ to						
100 parts H₂O,	57.88	61.78	64.01	67.12	69.93	72.33
Temperatures,	30°	35.5°	40°	45°	48°	52°	56°
Parts MnSO₄ to						
100 parts H₂O,	74.67	78.81	79.63	83.06	84.33	86.16	88.19

[1] *Loc. cit.*

Tri-hydrate: $MnSO_4.3H_2O$.

Graham states that " a crystalline crust of sulphate of manga-
nese, deposited from a warm solution, was found to contain three
atoms of water." No other mention, so far as I know, has been
made by any investigator of the spontaneous crystallization of the
tri-hydrate from solution. Brandes[1] affirms that he obtained the
tri-hydrate by the decomposition of other hydrates. Thus by
boiling absolute alcohol over the hepta-hydrate as well as over
the tetra-hydrate, he succeeded in reducing the number of mole-
cules of water combined with the salt to three. I myself have
found that if 98-per cent. alcohol be poured over the tetra-hydrate,
and the whole be allowed to stand at $\pm$ 20°, the clear crystals of the
tetra-hydrate gradually become opaque and fall apart to form a
powder. An analysis made at the end of a month gave results
corresponding with the formula $MnSO_4.3H_2O$. I made a couple
of determinations of the solubility of the hydrate thus obtained,
finding them to coincide with those made with the tri-hydrate as
described below. Brandes assumes that the tri-hydrate is formed
when the tetra-hydrate is exposed in a vacuum for some time to
the dehydrating action of sulphuric acid or calcium chloride.

Brandes' statement that dehydrated manganous sulphate grad-
ually absorbs three molecules of water from the air, I can in nowise
corroborate. In general it may be said that the amount of water
that a dehydrated salt can absorb from the air is a function of the
temperature and the hygroscopic condition of the atmosphere ;
the higher the temperature and the drier the air, the less the quan-
tity of water taken up by the salt. If at ordinary temperatures
the salt be exposed to an atmosphere always saturated with aqueous
vapor, it will in time absorb enough water to dissolve itself. It is
accordingly inaccurate to affirm that a definite hydrate is formed.
True, the conditions of moisture and temperature may be such
that the salt will after a time lose about as much water as it absorbs,
and the composition of the mixture may correspond to that of a
definite hydrate, but we cannot therefore conclude that such a
definite hydrate has been formed. To illustrate these consider-
ations in the case of manganous sulphate, a weighed quantity of
the carefully dehydrated salt was put on a watch-glass placed on a
support in a large beaker. Some water was poured into the beaker,
which was then tightly closed with a glass plate. The salt was

[1] *Loc. cit.* p. 574.

thus exposed to an atmosphere saturated with aqueous vapor. The beaker was then set in a place where the temperature did not vary much from 20°, and the watch-crystal and its contents weighed from time to time. Table VI gives the weights after the times specified.

TABLE VI.

Absorption of Moisture by $MnSO_4$.

Hours,	0	3	20	43	60	110
Weight of salt in grams,	2.4176	2.4561	2.6173	2.8285	3.4126	4.9108

After about 100 hours, enough water had been absorbed to dissolve the salt.

The tri-hydrate is formed on slowly heating a solution over the hepta-hydrate above 7° up to 35°. It is easily obtained in quadratic crystals by allowing a solution to evaporate at 33°–35°.

Table VII gives the results of the determinations of its solubility, which are represented graphically in Fig. 2 (curve 3, 3).

TABLE VII.

Solubility of $MnSO_4.3H_2O$.

Temperatures,	5°	12°	16°	19°	25°	30°
Parts $MnSO_4$ to 100 parts H_2O,	54.68	60.56	63.41	65.12	66.85	67.38
Temperatures,	35°	40°	48°	53°	57°	
Parts $MnSO_4$ to 100 parts H_2O,	68.31	70.63	71.89	72.81	73.17	

Di-hydrate : $MnSO_4.2H_2O$.

By heating the hepta-hydrate slowly with 55-per cent. alcohol to about 80°, Brandes[1] states he got a "weissen, opaken Krystallmehl," which had a composition corresponding to that of the di-hydrate. I regard it as doubtful, however, that the di-hydrate can exist at that temperature. Probably he did not succeed in removing all moisture from the compound before analyzing it.

The di-hydrate may easily be obtained in rhombic crystals by evaporating a solution of manganous sulphate on a water-bath until a crust begins to form on the top. It is then exposed to the temperature $\pm 43°$ in the thermostat. The solution must be

[1] *Loc. cit.*

stirred from time to time so that the pinkish crust that forms may be made to settle to the bottom. By sowing some of these crystals in a solution at 40°–45°, well-formed crystals can be obtained.

The di-hydrate was also obtained as a pinkish powder by the action of strong sulphuric acid upon solutions of manganous sulphate. If sulphuric acid (sp. gr. 1.83) be carefully run upon an equal volume of a 70-per cent. solution of manganous sulphate in alcohol, a precipitation of a pinkish-white powder takes place. The mixing of the acid and alcohol must take place slowly—by diffusion alone—that too much heat be not evolved. After two or three days the separation of the di-hydrate is completed. The solution is then filtered through glass-wool with the aid of a suction-pump, and the precipitate washed with 50-per cent. alcohol. A determination of water in the hydrate (which was well dried by pressing between folds of filter-paper) gave 19.54 per cent. H_2O, while the di-hydrate contains 19.21 per cent. The solubility of the di-hydrate is given in Table VIII, and represented graphically in Fig. 2 (curve 2, 2).

TABLE VIII.

Solubility of $MnSO_4.2H_2O$.

Temperatures,	35°	40°	42°	45°	50°	55°
Parts $MnSO_4$ to						
100 parts H_2O,	68.88	75.31	77.63	80.07	83.16	86.27

Mono-hydrate : $MnSO_4.H_2O$.

Solutions of manganous sulphate containing more than 70 per cent. of salt deposit at temperatures from 60° to 70° a whitish solid. Thus it is that on boiling solutions of manganous sulphate they become turbid from the separation of solid matter. Analysis proves this compound to be the mono-hydrate. The fact that manganous sulphate is more soluble at temperatures below 60° than at temperatures above that point has been known for a long time. The first analysis of the precipitate was made by Kühn ;[1] Étard[2] also gives the results of an analysis.

By boiling the tetra-hydrate with 90-per cent. alcohol, the mono-hydrate is easily obtained as a pinkish-white powder. It is diffi-

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[1] J. prakt. Chem. **61**, 239.   [2] Compt. rend. **106**, 208.

cult to separate it from its aqueous solution, the solution being so thick and the precipitate so fine that filtration is out of the question. The mono-hydrate was also obtained in the following way: A 70-per cent. solution of manganous sulphate was heated in the thermostat to 47°, and an equal volume of 98-per cent. alcohol added. Two layers soon separated out;[1] in a day or so a quantity of hard pinkish crusts were deposited in the lower layer, and these consisted of the mono-hydrate.

The results of the determination of its solubility are recorded in Table IX, and shown graphically in Fig. 2 (curve 1, 1).

TABLE IX.

Solubility of $MnSO_4.H_2O$.

Temperatures,	48°	53°	65°	72°	78°
Parts $MnSO_4$ to					
100 parts H_2O,	87.98	86.10	84.33	82.73	79.13
Temperatures,	90°	100°	106°	115°	117°
Parts $MnSO_4$ to					
100 parts H_2O,	75.63	71.27	70.14	69.78	68.81

Dehydrated Manganous Sulphate.

Étard[2] has determined the solubility of dehydrated manganous sulphate from —8° to 57°. At —8°, " le sulphate de manganèse anhydre et l'eau sont dans le rapport moleculaire $SO_4Mn : 19H_2O$; à 57°, on a $SO_4Mn : 9H_2O$." Now my determinations of the solubility of the hepta-hydrate at —8° show the anhydrous salt and water to be in the molecular ratio $MnSO_4 : 19H_2O$; and at 57°, if the determination be made with solution over the tri-hydrate, the ratio is $MnSO : 10H_2O$. These results agree with those of Étard, and the cause of the agreement is not far to seek. Anhydrous manganous sulphate rapidly takes up seven molecules of water at —8°; Étard's determination then is that of the hepta-hydrate. As stated above (p. 236), the hepta-hydrate easily decomposes into the tri-hydrate, so that Étard's determination at 57° was with the tri-hydrate. His method of determining solubilities[3] is such that it

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[1] It is noteworthy that the color of the lower layer was much less intense than that of the original solution, showing that the electrolytic dissociation was not so great as before.

[2] Compt. rend. **106**, 208.

[3] Sur la Solubilité des Sels : Conference faite au laboratoire de M. Friedel, 1888-1889, page 136.

is possible for such changes in the amount of water of crystalliza-
tion to occur. Now if it be remembered that Étard expressed
the results of his determinations of solubility in parts of salt to 100
parts of saturated solution, and that the effect of such a mode of
representation is to straighten out curves, it is apparent that his
results coincide closely with mine as given in Table II.

In Table X are given the results of the determinations of the
solubility of anhydrous manganous sulphate which are platted
in Fig. 2.

TABLE X.

Solubility of the Dehydrated Sulphate.

Temperatures,	120°	132°	141°	146°	155°	170°
Parts MnSO₄ to						
100 parts H₂O,	67.18	63.16	41.18	38.83	26.49	16.15

Discussion of Curves (Fig. 2).

The curves of solubility of the hydrates of manganous sulphate
regarded collectively present certain peculiarities. One which at
once attracts the attention is that five of them are concave towards
the axis of abscissæ. Consequently, the solubilities of the hexa-,
penta-, tetra-, tri- and di-hydrates do not increase so rapidly as
the temperature. On the other hand, the curves of the mono-hy-
drate and anhydrous salt are convex towards the axis of abscissæ,
their solubility diminishing less rapidly than the temperature rises.
The curve of solubility of the hepta-hydrate appears to be very
slightly convex towards the axis of abscissæ. This concavity of
the curves towards the axis of abscissæ has been found to occur
but rarely in the salts hitherto investigated.

Another peculiarity is the relative position of the curves. Con-
sidering the hexa-, penta-, tetra- and tri-hydrates, we observe the
more water of crystallization the hydrate contains, the greater its
solubility. Now the contrary is generally the case with the differ-
ent hydrates of other salts examined up to date.

Manganous sulphate has the property of uniting with water to
form "crystallo-hydrates" between the temperatures —10° and
117°; below the former temperature, a mechanical mixture of the
hepta-hydrate and ice separates out; above the latter temperature,
only the anhydrous salt is capable of existence. As the amount of
water of crystallization in the hydrates seems in the main to depend

upon the temperature, this interval of 127° may be divided into seven intervals, to each of which one of the hydrates corresponds. These we shall call the intervals of stable existence, or of stability of the hydrates. They are characterized by two circumstances:
1. A solution of manganous sulphate, kept at a temperature within one of these intervals, deposits the corresponding hydrate;
2. Any hydrate put with its solution at a temperature comprised within the limits of an interval of stability, passes more or less rapidly into the hydrate corresponding to the interval. Of course, the limits of these intervals of stability can be only roughly outlined, no sharp lines of demarcation existing between them; yet this conception of an interval of temperature in which a single hydrate is stable introduces a certain order which facilitates greatly the study of the hydrates. The limits of each of the hydrates are as follows:

For the hepta-hydrate, —10° to —5°,
   "   "   hexa-hydrate, — 5° to +8°,
   "   "   penta-hydrate,   8° to 18°,
   "   "   tetra-hydrate, 18° to 30°,
   "   "   tri-hydrate, 30° to 40°,
   "   "   di-hydrate, 40° to 57°,
   "   "   mono-hydrate, 57° to 117°.

It might be well before passing to the consideration of each of these hydrates, to make a few general remarks about heterogeneous systems and Gibb's rule of phases, of which this investigation is an illustration. Our heterogeneous system consists of the two definite compounds, manganous sulphate and water. If we consider a hydrate, the tri-hydrate, for instance, in equilibrium with its solution at a certain temperature, say 30°, we have three phases of the system before us. These are (1) aqueous vapor (gaseous); (2) solution (liquid); (3) tri-hydrate (solid).

At 37°, however, the tri-hydrate decomposes into water and the di-hydrate. 37° marks, therefore, a quadruple point of transition, where four phases can coexist, which are (1) aqueous vapor (gaseous); (2) solution (liquid); (3) tri-hydrate (solid); (4) di-hydrate (solid).

Similar considerations obtain for the other hydrates. Wherever two curves cross one another, there are four phases present, and a quadruple point of transition is thereby marked. In the

example above cited we have passed along the curve of the tri-hydrate until we arrived at the curve of the di-hydrate. There is, however, a quadruple point of transition between the mono-hydrate and tri-hydrate, occurring when the tri-hydrate is rapidly heated. There is a distinction to be made between these two points of transition; the one between the di- and the tri-hydrate is reversible, while the one between the mono- and the tri-hydrate is irreversible. That is, we arrive at the same point no matter whether we pass up the curve of the tri-hydrate or pass down the curve of the di-hydrate, while we arrive at the point of transition of the tri-hydrate and the mono-hydrate, only in passing up the curve of the tri-hydrate. The mono-hydrate does not pass directly into the tri-hydrate. Examples of irreversible points of transition are common with the hydrates of salts which possess a considerable stability.

The curve of solubility of the hepta-hydrate was determined from —10°, the cryohydratic point, to 7°, the temperature at which the hydrate ceases to be capable of existence. On heating the hepta-hydrate, partial melting occurs, that is, the hydrate loses water and is converted into lower hydrates. If the curves of solubility of the hexa-, penta-, and tetra-hydrates be prolonged downwards, they cut the curve of the hepta-hydrate at —5°, —2° and 0° respectively. All these temperatures are, however, within the interval of stable existence of the hexa-hydrate. The penta-hydrate at —2°, and the tetra-hydrate at 0°, are then in mobile equilibrium, both tending to pass into the hexa-hydrate. So soon as the hepta-hydrate might become changed into the penta- or tetra-hydrate, the latter would at once pass into the hexa-hydrate. Brandes[1] observed that at temperatures about 6° the hepta-hydrate decomposed into the hexa-hydrate: a fact entirely in accordance with the above statements. The upper limit of existence of the hepta-hydrate touches the curve of the tri-hydrate; the hepta-hydrate there decomposes into four molecules of water and the tri-hydrate. It must not be inferred, however, that the tetra- and penta-hydrates cannot be obtained by the decomposition of the hepta-hydrate, for such a transformation often takes place. But the transformation is not direct, that is, the hepta-hydrate does not lose all at once two or three molecules of water, as the case may be. If the hepta-hydrate with its solution be exposed to the tem-

[1] *Loc. cit.*

perature of 20°, the tetra-hydrate is finally obtained. The transformation may proceed in two ways: 1. The hepta-hydrate is converted into the hexa-hydrate, this into the penta-hydrate, and this finally into the tetra-hydrate; or, 2. the hepta-hydrate may be decomposed directly into the tri-hydrate, which then takes up a molecule of water, since it is in the interval of stable existence of the tetra hydrated salt. The product of the decomposition depends chiefly upon the interval of stability taken. Similar considerations are applicable for the transformation of the hepta-hydrate into other hydrates.

The hexa-hydrate seems to be incapable of existence at temperatures below —5°, the point at which its solubility crosses that of the hepta-hydrate. From this point, the curve rises rapidly at first, then more and more slowly. At temperatures from 30° to 35° it decomposes rapidly into the tetra-hydrate. As these temperatures are within the limits of the interval of the tri-hydrate's interval of stability, one would expect that the tri-hydrate would be the product of its decomposition. There seems to be a great reluctance, however, on the part of the hexa-hydrate to pass into the tri-hydrate; it seems to be easier for it to become converted into the tetra-hydrate, even when this hydrate is not in its interval of stability. Perhaps the considerable difference of solubilities is of influence on the kind of transformation undergone.

The curve of solubility of the hexa-hydrate cuts that of the penta-hydrate at 15°, a temperature within the interval of stability of the latter hydrate. The hexa-hydrate should yield the penta-hydrate then, if kept long enough at that temperature, and such has been found to be actually the case. A solution of the hexa-hydrate was maintained at 14°–15°, and samples of the crystals removed from day to day and analyzed. The amount of water of crystallization found did not correspond to that of the penta-hydrate until the seventeenth day.

The penta-hydrate and the tetra-hydrate at temperatures near zero pass into the hexa-hydrate. To determine the rapidity with which this transformation takes place, solutions of the penta- and of the tetra-hydrate were exposed side by side to the temperature of melting ice. These were shaken frequently and their concentrations determined (1) after three hours, (2) after six hours, (3) after nineteen hours, (4) after thirty hours. The concentration of each did not coincide with the solubility of the hexa-hydrate until after 20–30 hours.

The curves of solubility of the penta-hydrate and of the tetra-hydrate are nearly parallel, not crossing each other at any point. This indicates that there exists some similarity in the relations of these hydrates to the other hydrates. As stated above, both pass with about the same velocity into the hexa-hydrate at temperatures near zero. Likewise, at temperatures above 35° both easily pass into the di-hydrate. By heating a saturated solution of the penta-hydrate rapidly, it does not decompose into the mono-hydrate before the temperature 58° is reached; similarly, the tetra-hydrate may be heated to 61° before the mono-hydrate appears. In no case have I observed that either the tetra-hydrate or the penta-hydrate became converted into the tri-hydrate.

As might be expected, the tetra- and penta-hydrates are mutually transformable only with great difficulty. A solution of the penta-hydrate was kept at 25° for a couple of weeks without the hydrate's losing water of crystallization. On raising the temperature to 30°, the transformation was complete in 50 hours. This shows that such a transformation is possible only at the upper limit of the interval of stable existence of the tetra-hydrate. In like manner, the conversion of the tetra-hydrate into the penta-hydrate is possible only at the lower limit of the interval of stability of the penta-hydrate. Thus, by maintaining a solution of the tetra-hydrate at 9°–10°, I found the concentration of the solution after a week or so to coincide with the solubility of the penta-hydrate. This want of readiness on the part of the penta- and the tetra-hydrate to pass into each other is further illustrated by the facts that, if crystals of the tetra-hydrate be sown in a super-saturated solution of manganous sulphate at 13°–14°, the tetra-hydrate crystallizes out, although the temperature is within the limits of stability of the penta-hydrate; and if crystals of the penta-hydrate be sown in a supersaturated solution, even at so high a temperature as 25°–26°, a growth of the crystals of the penta-hydrate occurs. After some time, however, the hydrates belonging in the intervals of stability are formed.

The solubility of the tri-hydrate is less than that of the three next higher hydrates, and its curve is seen to be quite independent of theirs, not crossing them at all. There are, then, no points of transition between the hexa-, penta-, and tetra-hydrates and the tri-hydrate, and this is the reason why the latter hydrate does not pass into the penta- or the tetra-hydrate at all easily, and why the

hexa-hydrate at higher temperatures breaks up into the tetra-hydrate rather than into the tri-hydrate. At temperatures within the interval of stable existence of the hexa-hydrate, however, the tri-hydrate passes rapidly into that hydrate. The di-hydrate transforms itself so readily into the tri-hydrate, when it is within the interval of stable existence of this hydrate, that its solubility could be determined only down to the temperature 35°. From this point its curve of solubility rises rapidly to 57°, where the mono-hydrate appears. Not being capable of existence within the intervals of stability of the hydrates higher than the tri-hydrate, its curve has no relations with theirs.

The curve of solubility of the mono-hydrate is essentially different from the curves of the other hydrates, since the mono-hydrate is more soluble in cold than in hot water. I have not been able to determine its solubility at temperatures below 40°, because higher hydrates promptly separate out from such concentrated solutions. In more dilute solutions, the transformation of the mono-hydrate takes place more slowly. Thus, a solution of manganous sulphate was evaporated at 100°, until a quantity of the mono-hydrate had separated out. This was exposed to a temperature of 18°–20°. In a few days, rhombic crystals of the tetra-hydrate appeared, which grew gradually while the amount of the mono-hydrate diminished. As the transformation proceeded, the white, powdery mono-hydrate collected together so as to form ill-defined rhombs, which finally became regular and transparent. The directive force of the act of crystallization made the loose powder assume the geometrical form characteristic of the tetra-hydrate.

At 117° the mono-hydrate loses its water of crystallization, and above that temperature the anhydrous salt is alone stable. The curve expressing its solubility is very steep and convex towards the axis of abscissæ, which it cuts at about 180°. Above this temperature, then, manganous sulphate is insoluble in water. Étard[1] has indeed found " qu'une solution de sulphate de manganèse chauffée à 180° ne contient plus que des quantités negligeables matière en solution." Anhydrous manganous sulphate combines with one molecule of water of crystallization with great ease. Thus, crusts of the dehydrated salt were added to a solution kept at 60° and of such a concentration that the mono-hydrate just

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[1] Compt. rend. **106**, 208.

began to separate out; the crusts fell apart very soon to form the characteristic powdery mono-hydrate, as proven by analysis. The combination of the anhydrous salt with more molecules of water than one, takes place with much more difficulty.

It is interesting to follow out the changes in the direction of the curves due to the combination of molecules of water with the anhydrous salt to form hydrates. Thus, beginning at 180°, as the temperature falls, manganous sulphate rapidly enters into solution. At 117° the anhydrous salt combines with one molecule of water, and immediately there is a break in the continuity of the curve. The solubility of the mono-hydrate also increases with falling temperature until the temperature 57° is attained. Here the di-hydrate appears, and the direction of the curve changes completely, the solubility decreasing as the temperature falls. Passing down the curve of solubility of the di-hydrate we arrive at the temperature 37°, where another molecule of water adds itself to the di-hydrate and we have to do with the curve of solubility of the tri-hydrate. This ends at 7°, where it joins the curve of the hepta-hydrate. The curve of the hepta-hydrate ends at —10°, the cryohydratic point.

The general course of these curves resembles the theoretical curve of solubility given by Le Chatelier.[1] It is to be observed that we have not found it necessary in passing from the anhydrous to the hepta-hydrated salt, to take into consideration the hexa-, penta-, or tetra-hydrates. They seem to occupy a position apart from the others. Accordingly, we have two sets of curves: one composed of the hepta-, tri-, di-, and mono-hydrates, and the other of the hexa-, penta-, and tetra-hydrates. These two sets seem to be quite independent of each other.

Supersaturated Solutions.

The term "saturation" is indefinite unless referred to a distinct nucleus, which may be a hydrate or an anhydrous substance. Saturation is not a property of solutions, but a state of equilibrium between solid and solution. Supersaturation is therefore a relative term. A solution may be supersaturated with respect to one hydrate of a salt, and "undersaturated," if such an expression be allowable, with respect to another. The hydrates of manganous

[1] " Recherches experimentelles et théoriques sur les équilibres chimiques," page 139. See also Ostwald's " Lehrbuch der Chemie," **I**, 1057.

sulphate illustrate well these statements. At 10°, for instance, it is possible to prepare four different solutions, saturated with hexa-, penta-, tetra- and tri-hydrate respectively. A solution containing between 68 and 70 parts of salt is supersaturated only with respect to the penta-, tetra- and the tri-hydrates. A solution containing 65 parts of the salt is supersaturated only with respect to the tetra- and tri-hydrates. If now a crystal of any of these three lower hydrates be introduced into a saturated solution of the hexa-hydrate, a separation of crystals of the hydrate added should occur. Accordingly, a solution saturated with the hexa-hydrate should, if a crystal of the penta-hydrate be thrown into it, deposit the penta-hydrate. The weakened solution would now dissolve more of the hexa-hydrate, and this would continue until all the hexa-hydrate was converted into the penta-hydrate. Similar considerations obtain for the other hydrates.

But we have left out of consideration the influence of temperature. The transformation of the hexa-hydrate into the penta-hydrate is possible only when the solution is at a temperature within the interval of stable existence of the penta-hydrate. If it be at a temperature comprised in the interval of the hexa-hydrate, the penta-hydrate may indeed at first crystallize out, but it will soon unite with a molecule of water, and nothing but hexa-hydrate will be present. Also, if a crystal of the penta-hydrate be sown in a solution of the hexa-hydrate, and the whole at once be raised to a temperature within the interval of stability of the di-hydrate, whatever penta-hydrate that may have formed, as well as all the hexa-hydrate, will change into the di-hydrate.

Heat of Solution.

A most important law having reference to the relation of temperature to solubility was enunciated at about the same time by Le Chatelier[1] and by van't Hoff.[2] It states that the solubility of substances which dissolve " in saturated solution " with absorption of heat increases with rise of temperature, while it diminishes with rising temperature if heat is evolved in the act of solution. Its mathematical expression is

$$\frac{dp}{dT} = \frac{\rho}{Tv} \, ,$$

in which p represents the osmotic pressure which is approximately

[1] Compt. rend. **100**, 441   [2] Arch. néerland. **20**, 53.

proportional to the concentration,[1] T the absolute temperature, ρ the heat of solution, and v the volume of the solution.

According to this law, the heat of solution of manganous sulphate should be positive for the mono-hydrate, and negative for the other hydrates. This conclusion can easily be verified in the case of the mono-hydrate.

Thomsen[2] has found that the tetra- and penta-hydrates dissolve in water with evolution of heat:

$$\text{``} MnSO_4 + 5H_2O + 400\ H_2O = +\ 40\ c.$$
$$MnSO_4 + 4H_2O + 400\ H_2O = +\ 1770\ c.\text{''}$$
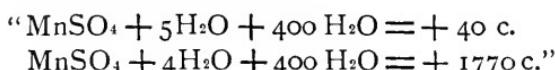
and calls particular attention to this unusual case. But a fundamental distinction must be made between the various meanings of the term "heat of solution." The true heat of solution is the heat given out or taken in when a solution passes from a state of saturation at a certain temperature to a state of saturation at a temperature infinitely near the other. This is the heat of solution for which the above law holds good. If more water be added to the saturated solution, heat may be evolved or absorbed, and we have to do with the heat of dilution. Now the true heat of solution may be negative and the heat of dilution positive. In that case there must be a concentration for which no heat is evolved or absorbed when a fresh portion of substance enters into solution. Thus it is possible to dissolve a substance in such a quantity of solvent that the heat effect is *nil*. In the above thermochemical determinations of Thomsen, the hydrates are dissolved in such a quantity of water that further dilution does not bring about a thermal change. In the majority of salts the heat of dilution is small compared with the heat of solution. Just the opposite behavior is observed in the case of the penta- and tetra-hydrates of manganous sulphate. Their true heat of solution is undoubtedly negative, while their heat of dilution is positive. Accordingly, by diluting a saturated solution of either of these hydrates, at a certain point the sign of the heat that comes into play changes from negative to positive. I have found that a solution of the sulphate containing 70 parts of anhydrous salt to 100 parts of water (the concentration of a saturated solution of the tetrahydrate at 20°) when exposed to temperature of 25°, dissolves more of the tetra-hydrate with a slight absorption of heat, a result entirely in accordance with the above law.

[1] See, however, Ztschr. phys. Chem. **9**, 43.   [2] Ber. d. chem. Ges. **6**, 711.

THE PRODUCTS OF THE CONDENSATION OF ACETONE WITH CONCENTRATED SUL-PHURIC ACID.[1]

By W. R. Orndorff and S. W. Young.

Historical.

The action of sulphuric acid on acetone was first studied by Sir Robert Kane.[2] He distilled two volumes of acetone with one of concentrated sulphuric acid and obtained, as the principal product of the reaction, a hydrocarbon to which he gave the name mesitylene and for which he deduced the formula C_3H_4 from his analyses. The other products he mentions were mesitic ether and a white waxy substance. These were probably the substances we now know as mesityl oxide and phoron. Kane regarded acetone as an alcohol, and explained the reaction by assuming that acetone, or mesityl alcohol as he called it, formed mesitylene by the loss of one molecule of water, according to the equation

$$C_3H_6O - H_2O = C_3H_4,$$

just as ethyl alcohol yields ethylene under similar conditions.

Hofmann[3] and, later, Cahours,[4] showed that the formula of mesitylene is C_9H_{12}. Hofmann points out that three molecules of acetone condense to one of mesitylene, and calls attention to the resemblance of this reaction to the transition of cyanic acid into cyanuric acid, etc. He continues: "The natural product, too, which we should expect from the dehydration of acetone is a substance of the formula C_3H_4, and it is not improbable that this compound is actually formed at a certain stage of the process; under the influence, however, of the powerful agent in the presence of which it is generated, we find it rapidly converted into a compound containing the triple number of equivalents."

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[1] An abstract of this paper was read before the Chemical Section of the American Association for the Advancement of Science at the Rochester meeting.

[2] On a Series of Combinations derived from Pyroacetic Spirit. Graisberry, Dublin, 1838; J. prakt. Chem. (1838) **15**, 129; Ann. der Phys. Pogg. **44**, 473.

[3] Ann. Chem. (Liebig) **71**, 121; Q. J. Chem. Soc. **2**, 104.

[4] Ann. Chem. (Liebig) **74**, 107.

Fittig[1] and his pupils made a thorough study of the reaction between acetone and sulphuric acid, and showed, from its conduct on oxidation, that mesitylene contained three methyl groups. The method of preparation of mesitylene finally adopted by Fittig[2] was as follows: Two volumes of sulphuric acid, previously diluted with one volume of water, are slowly added to a mixture of crude acetone and sand contained in a large retort. The mixture is allowed to stand for twenty-four hours and is then distilled. The crude mesitylene thus obtained is separated from the aqueous layer, washed with a solution of caustic soda and subjected to fractional distillation. By this methed he succeeded in obtaining 100 grams of mesitylene from three pounds of acetone. Fittig states that gases are evolved during the reaction: sulphur dioxide in considerable quantity, and with it a gas which smelled like allylene (methyl acetylene). The reaction expressing the condensation of acetone to mesitylene he writes as follows:

$$3C_3H_6O - 3H_2O = C_9H_{12}.$$

He explains this reaction by assuming that by the action of sulphuric acid on acetone, allylene is first formed according to the equation
$$C_3H_6O - H_2O = C_3H_4,$$

and that this allylene thus formed undergoes polymerization in the presence of the sulphuric acid, resulting in the formation of mesitylene. Mesitylene he considers as triallylene, and thinks that perhaps it may be possible to isolate also a diallylene, C_6H_8, from among the products of the reaction.

Holtmeyer,[3] working with Fittig, showed that mesityl oxide, boiling at 128°–130°, prepared from commercial acetone, when mixed with one-half its volume of strong sulphuric acid, and distilled, after the mixture had been allowed to stand two days, gave two hydrocarbons: mesitylene, boiling at 163°–166°, and another hydrocarbon boiling at 195°. He regards mesityl oxide as an intermediate product between acetone and mesitylene. The product boiling at 195° is more easily obtained, according to Holtmeyer, from the residues obtained in the preparation of mesitylene, especially if one lets the mixture of acetone and sulphuric acid stand for some time before distilling. This hydrocarbon is con-

[1] Ann. Chem. (Liebig) **141**, 129.   [2] *Ibid.* **147**, 42.
[3] Ztschr. Chem. 1867, 683.

taminated with sulphur compounds, (mercaptans), from which it is purified by repeated distillation over sodium. When pure it was found to have the composition $C_{10}H_{14}$. With bromine it gave a compound crystallizing from alcohol in needles. This bromine derivative melted between 196° and 202°, and on analysis gave figures corresponding approximately to the formula $C_{10}H_{12}Br_2$. With fuming nitric and sulphuric acids Holtmeyer claims to have obtained a nitro-compound which gave figures on analysis corresponding to the formula $C_{10}H_{11}(NO_2)_3$. The barium salt of the sulphonic acid he states corresponds in the amount of barium to the formula $(C_{10}H_{13}SO_3)_2Ba$. This barium salt was tolerably soluble in water and crystallized in shining needles. Holtmeyer in no case gives the results obtained in his analyses.

Baeyer,[1] in 1866, in a paper On the Condensation Products of Acetone, pointed out that Fittig's work together with his own showed that mesitylene was a trimethylbenzene, and deduced the symmetrical formula for mesitylene, regarding it as benzene in which three methyl groups were symmetrically placed.

O. Jacobsen[2] modified Fittig's method and obtained 110 grams of mesitylene from 1 kilogram of acetone. He found that when large quantities of mesitylene were prepared from acetone and sulphuric acid, he obtained in small quantity a hydrocarbon boiling at about 200°. From the analyses of the barium salt[3] of its sulphonic acid he first thought it was a tetramethylbenzene. He states that Fittig and Bruckner[4] had later obtained a hydrocarbon in the preparation of mesitylene, boiling at 194° to 196°, for which they regard the formula $C_{10}H_{14}$ as probable, and that H. Rose[5] had called attention to the fact that on dissolving crude mesitylene in warm fuming sulphuric acid a sulphonic acid is formed in small quantity which gives a difficultly soluble barium salt, the barium salt of mesitylene-sulphonic acid being quite soluble. Jacobsen then states that if pure acetone be used in the preparation of mesitylene, no higher-boiling products than mesitylene are formed, but that, if the acetone contain higher-boiling products, the mesitylene made from it will contain higher hydrocarbons. His exact words are as follows: " Ich habe bei späteren Darstellungen des Mesitylens widerholt beobachtet, dass bei Anwendung von ganz reinem Aceton keine Spur eines höheren Kohlenwasserstoffes

[1] Ann. Chem. (Liebig) **140**, 297.   [2] Ber. d. chem. Ges. **7**, 1432.
[3] Ann. Chem. (Liebig) **146**, 101.   [4] *Ibid.* **147**, 44.   [5] *Ibid.* **164**, 54.

gebildet wird, dass dagegen, wenn das Aceton höher siedende Verunreinigungen enthielt auch das daraus bereitete Mesitylen mit oft nicht unerheblichen Mengen höherer Kohlenwasserstoffe verunreinigt ist." He explains the formation of the hydrocarbons with higher boiling-points by assuming the presence in the acetone used of methylethylketone. Fittig,[1] he states, has already shown that methylethylketone is a constituent of crude acetone, and he himself shows that mixtures of methylethylketone and acetone, when treated with concentrated sulphuric acid and subjected to distillation according to Fittig's method for the preparation of mesitylene, give three hydrocarbons having a higher boiling-point than mesitylene. One of these, boiling at 180° to 184° (corr.), he shows to be 1, 3, 5 dimethylethylbenzene, and the others, boiling at 198° to 200° and 217° to 220°, to be 1, 3, 5 diethylmethylbenzene and 1, 3, 5 triethylbenzene, respectively. He considers the hydrocarbon which he earlier obtained from the crude mesitylene by fractional distillation and which boiled at about 200°, to be identical with the diethylmethylbenzene, obtained from mixtures of acetone and methylethylketone, and not with tetramethylbenzene, as he first stated.[2] The analyses of the barium salt of the sulphonic acid made from this hydrocarbon he states give numbers which agree better with the formula $(C_{11}H_{15}=SO_3)_2Ba$ than with the formula $(C_{10}H_{13}SO_3)_2Ba$. The hydrocarbon mentioned by Fittig and Bruckner and, later, by Holtmeyer, which boiled at 194° to 196° and which was obtained from the crude mesitylene, he is inclined to believe is identical with this diethylmethylbenzene.

In an article entitled On the Action of Sulphuric Acid on Allylene,[3] Fittig and Schrohe showed that concentrated sulphuric acid absorbs large quantities of allylene, and that this solution, when diluted with a small quantity of water and subjected to distillation, not only gave mesitylene, but that the solution exhibited on heating all of the properties shown by a mixture of acetone and sulphuric acid when heated, and gave off the same odor. When the solution of allylene in sulphuric acid is diluted with more water than was first used, and the mixture distilled, a considerable quantity of acetone was found in the distillate. These experiments were afterwards repeated[4] with larger quantities of sulphuric acid and allylene, and the earlier observations found to be correct. The

[1] Ann. Chem. (Liebig) **110,** 17.   [2] Ber. d. chem. Ges. **7,** 1435.
[3] *Ibid.* **8,** 17.   [4] *Ibid.* **8,** 367.

authors are inclined to think that when allylene is absorbed by sulphuric acid there is formed besides the stable allylenesulphonic acid, another very unstable sulphonic acid which is decomposed into acetone and sulphuric acid even on dilution with cold water. From the determination of the amount of barium in the barium salt of the stable sulphonic acid they deduce for it the formula $(C_3H_5SO_3)_2Ba$, which requires 36.53 per cent. of barium, while they found 36.24 per cent. They give neither figures nor weights, do not state whether the barium salt was crystallized or not, and made no other determination than that of barium.

Claisen[1] in 1876 showed that mesitylene was formed directly from acetone by the action of sulphuric acid, and that mesityl oxide and phoron were by-products of the reaction, and not intermediate products. He sums up his results in these words : " Dass der Bildung des Mesitylens aus den Condensationsproductes des Acetons ein Zerfallen derselben in Aceton, resp. in Derivate desselben, vorhergeht. Mesityloxyd und Phoron sind keine Zwischenproducte der Mesitylenbildung. Das neben dem Mesitylen auftretende Mesityloxyd hat nur die Bedeutung eines neben, nicht aber eines Zwischenproductes."

Regarding the way in which the formation of mesitylene from acetone takes place, whether by direct union of three molecules of acetone with loss of three molecules of water, without previous condensation to mesityl oxide or phoron ; or by the polymerization of the allylene, which is first formed, as the experiments of Fittig and Schrohe make probable ; remains, he says, to be shown.

Bielefeldt,[2] in his inaugural dissertation published in 1880, reviews the various methods for the preparation of mesitylene, and states that he obtained only 100 grams of pure mesitylene from one and a half kilograms of technical or commercial acetone. In order to increase the yield he used pure acetone in the reaction, but found that he obtained no yield of mesitylene at all ; though sulphur dioxide, slight traces of mesitylene and water containing acetone distilled, the principal part of the acetone was charred. He says: "Reines Aceton mit Schwefelsäure behandelt gab also fast gar kein Mesitylen ; hieraus schloss ich, es sei in dem rohen Aceton ein Körper enthalten aus welchem entweder das Mesitylen entsteht, oder der ganz wesentlich zur Bildung

[1] Ann. Chem. (Liebig) **180**, 22.   [2] Ueber Isodurolsulfosäure, etc. Göttingen, 1880.

desselben beiträgt." Since crude acetone contains also methyl alcohol, he supposed that this body might be necessary to form mesitylene, and he tried treating various mixtures of acetone and methyl alcohol with sulphuric acid, but obtained no mesitylene, although he varied the experiments in several ways. By using commercial acetone he succeeded in preparing considerable mesitylene, by Fittig's method, without any further trouble.

W. H. Greene,[1] in 1880, decomposed acetone with zinc chloride at high temperatures and obtained saturated and unsaturated hydrocarbons, (principally propylene), and hexamethylbenzene.

Varenne,[2] in 1883, took up the question of the preparation of mesitylene. He states that Fittig's method gives a very small yield of mesitylene. He therefore first tried the action of chloride of zinc on acetone, but did not obtain any mesitylene. His best results were obtained by mixing 180 grams of acetone and 300 grams of sulphuric acid, and allowing the mixture to stand for one hour. He then distils the mixture, heating it very gently with a rose-burner. When the reaction begins and gas is given off, he passes in steam and lessens the heat or takes the burner away. The distillation in steam is then continued so long as drops of crude mesitylene continue to condense. From the 180 grams of acetone he obtained about 40 grams of crude mesitylene.

Meyer and Jacobson, in their Organic Chemistry (page 411) state on the authority of Bielefeldt in regard to this decomposition of acetone with sulphuric acid, " Es verdient bemerkt zu werden, dass nur aus käuflichem Aceton, nicht aus reinem Aceton durch Condensation mit conc. Schwefelsäure Mesitylen erhalten wird. Welche Beimenge des rohen Acetons für die Mesitylenbildung wesentlich ist, ist nicht aufgeklärt." If this statement be correct, it will be seen that the symmetrical formula for mesitylene, which Baeyer deduces from the condensation of three molecules of acetone to one of mesitylene with the loss of three molecules of water, will not hold, and that our views regarding the relation existing between acetone and mesitylene must be modified.

The following investigation was undertaken to determine, first, whether mesitylene is formed from pure acetone by condensation with sulphuric acid ; secondly, if any higher-boiling products than mesitylene are formed when pure acetone is used in the reaction ; thirdly, to determine what gases, if any, are given off; and, lastly,

[1] This Journal 2, 26.   [2] Bull. Soc. Chim. (Paris) 40, 267.

to determine how the reaction, which results in the formation of mesitylene, takes place, *i. e.* whether any intermediate products are formed.

Experimental.

The acetone used in this work was a remarkably pure specimen obtained from the Roessler and Hasslacher Chemical Co., of New York City. The process[1] by which this acetone is made is a patented one and consists in the dry distillation of purified calcium acetate at a low temperature, dry steam being admitted from time to time to regulate the temperature and the process of distillation. The distillate is then treated with milk of lime to remove tarry products and acids, and is then subjected, in the factory, to careful fractional distillation through long rectifying columns arranged on the plan of those used in the rectification of alcohol. A liter of this acetone thus prepared and purified was dehydrated by heating it to its boiling-point for half an hour with fused calcium chloride in a flask connected with a return-condenser. It was then separated from the calcium chloride and distilled. The whole quantity passed over between 55.6° and 56.2° C., the barometer indicating a pressure of 746 mm. The thermometer used was a standardized short Anschütz thermometer, and during the distillation the mercury column was entirely surrounded by the vapor of the boiling liquid. This acetone was shown to be free from dimethylacetal, for it gave no trace of methyl chloride when heated with concentrated hydrochloric acid. Had dimethylacetal been present it would have been decomposed by the hydrochloric acid, and methyl chloride would have been one of the products of the decomposition. That this acetone was free from methylethylketone (which boils at about 78°) may be regarded as certain from a consideration of its boiling-point.

The sulphuric acid used in the reaction was the ordinary colorless commercial concentrated sulphuric acid having a specific gravity of 1.82. Several weeks were spent in preliminary experiments to determine the best method of decomposing acetone with sulphuric acid and the best conditions. The method given by Varenne was followed out exactly in accordance with the conditions and quantities of materials he recommends. The average yield of crude mesitylene obtained by this method was 21.5

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[1] Patents (U. S.) 38577, July 11, 1888, and 393079, November, 1888.

grams to 180 grams of the acetone used. Various modifications of Varenne's method were then tried. It was found that the yield of crude mesitylene was much larger when the sulphuric acid was added drop by drop to the acetone from a separating funnel, and the flask containing the acetone was kept cold with ice-water and shaken constantly while the acid was being added, so as to obtain a uniform distribution and action of the acid on the acetone. By these modifications of Varenne's method not only was the yield of crude mesitylene increased, but less tar was formed, and the carbonizing effect of the sulphuric acid on heating was much lessened. If the mixture of sulphuric acid and acetone is to be distilled after standing one hour, as recommended by Varenne, then it was found better not to keep the flask cold during the mixing, and to add the acid to the acetone much more rapidly so as to hasten the reaction by the heat developed. The yield of crude mesitylene is much better, however, when the acid is added more slowly to the cooled acetone, as stated above, and the mixture allowed to stand for twenty-four hours at the temperature of the room. The smaller yield of crude mesitylene obtained when the acetone and acid are rapidly mixed results from the carbonizing action of the sulphuric acid on the acetone on heating, as well as from the evaporation of the acetone by the heat of the reaction. When the mixture of acetone and sulphuric acid has stood for twenty-four hours the odor of acetone disappears entirely. The liquid becomes dark reddish brown in color, thick and oily in consistency, and smells somewhat of mesityl oxide.

The apparatus made use of for the distillations consisted of a two-liter balloon-flask which was connected with a condenser and receiver on one side and on the other with a carbon dioxide generator and a steam-boiler. A thermometer dipping into the mixture of sulphuric acid and acetone serves to indicate the temperature of the reaction. When the gases evolved were to be collected, a tubulated receiver surrounded by a freezing mixture was used, and the gases passing from this were collected over strong caustic potash solution in a gas-holder arranged on the plan of a Schiff's nitrometer, with leveling bulb, mercury trap and exit-tube.

This gas-holder consisted of a liter round-bottom flask, with a long neck, turned bottom up. It was closed with a three-hole

rubber stopper. Through one hole passed a bent delivery-tube which held a small quantity of mercury in the bend to serve as a trap and prevent the running back of the caustic potash solution into the receiver owing to the absorption of carbon dioxide. Through the second hole passed the exit-tube. This was of small bore and reached to the top (bottom) of the flask. Through the third hole passed the tube which connected the flask with the leveling bulb. By raising or lowering this leveling bulb it was possible to increase or diminish the pressure at will. At the end of each distillation the gas collected in this holder was transferred to a larger one fitted up in exactly the same manner and, like it, filled with a strong solution of caustic potash (1 part of commercial caustic potash to 2 parts of distilled water).

Several experiments were made to determine whether the distillation in a current of steam increased the yield of crude mesitylene or not. The average yield of crude mesitylene when steam was used was found to be 33 grams to 180 grams of acetone used, but when steam was not used the yield fell to 21 grams of the crude mesitylene to the same quantity of acetone. It is probable that the steam acts here both mechanically and chemically : mechanically, by volatilizing the oil, and chemically, with the sulphuric acid present, by decomposing any sulphonic acids or ethereal salts of sulphuric acid present in the mixture. Miller[1] states in this connection that by distilling the sulphonic acids of the aromatic hydrocarbons the hydrocarbons are regenerated, and he adds that this decomposition is almost quantitative when the sulphonic acid or its salt is heated with an equal weight of oil of vitriol to 110°–170° and steam is conducted through the mixture.

Many experiments were made to determine the best proportions of sulphuric acid and acetone, but those given by Varenne were found to give uniformly the most satisfactory results.

The method of procedure was as follows : 180 grams of the acetone were placed in a 2-liter balloon-flask, the flask cooled with ice-water, and then 300 grams of concentrated sulphuric acid added gradually from a dropping-funnel, the flask being constantly shaken during the addition of the acid. When all the acid had been added the flask was allowed to stand at the temperature of the room for twenty-four hours. It was then connected with the

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[1] J. Chem. Soc. **45**, 148. *Cf.* Friedel and Crafts: Bull. **Soc. Chim.** (Paris) **42**, 66; and Kelbe: Ber. d. chem. Ges. **19**, 93.

condenser and carbon dioxide generator, and after all the air had been expelled, the receiver was connected with the gas-holder described above. The leveling bulb of this holder was then lowered to diminish the pressure, and the flask containing the mixture of sulphuric acid and acetone was heated slowly and gently on a sand-bath. At 120° C. the reaction begins. Sulphur dioxide is evolved in large quantities, and a gas begins to collect in the gas-holder. The temperature gradually rises even though the source of heat be removed, and finally reaches 140° C. When gas ceases to come off the gas-holder is disconnected from the receiver, and the distillation in steam is continued so long as any oil condenses in the receiver. About 100 cc. of gas collects in the holder, and the amount is about the same for each distillation. The liquid in the receiver consists of a lighter, oily, yellow layer (crude mesitylene) and a heavier, aqueous one, saturated with sulphur dioxide. These layers are separated and put aside until sufficient has been collected for examination. There remains in the distilling-flask an upper layer of a black, tarry substance, which partially solidifies on cooling to a thick mass resembling pitch and a lower layer of spent sulphuric acid. The total amount of acetone decomposed in the manner described above was 6.84 kilograms. This required 12.6 kilograms of sulphuric acid, gave 1.05 kilograms of crude mesitylene and nearly two liters of the aqueous layer. The products to be examined are, then, first, the gas ; second, crude mesitylene ; third, the tar ; fourth, the aqueous layer, and, fifth, the spent acid.

The Gas.—After sulphur dioxide and carbon dioxide had been completely removed, by passing some of the gas into a Hempel pipette filled with caustic potash solution, there remained a colorless gas which had a disagreeable odor (reminding one of the odor of illuminating gas), and which burned with a luminous, smoky flame. This gas was found to be slightly soluble in water, to which it imparted its odor, but much more readily soluble in alcohol. It was at first supposed to be allylene (methylacetylene), more especially since it was quite readily absorbed when allowed to stand for a short time in contact with fuming sulphuric acid in a Hempel sulphuric-acid pipette, and slowly decolorized a solution of bromine in water when left standing in contact with it. It was, therefore, passed through a small bulbed U-tube containing an ammoniacal solution of silver nitrate. But though the gas was

passed back and forth a number of times through this solution no absorption took place and not the slightest trace of a precipitate was formed. The U-tube was then filled with an ammoniacal solution of cuprous chloride, and the gas was passed back and forth through this solution a number of times. No absorption took place and no precipitate was formed. From these results it is obvious that no acetylene hydrocarbons were present. To decide this absolutely the reagent recommended by Béhal[1] for detecting the acetylene hydrocarbons was tried. This consists of a saturated alcoholic solution of silver nitrate. Since the reagent must not be present in excess, a small bulbed U-tube holding about 2 cc. was made and two-thirds filled with the reagent. Some of the gas was passed back and forth through this solution a number of times. About 14 per cent. of the gas taken was absorbed by the alcohol, but not the slightest trace of a precipitate could be observed. As this last reagent will detect the merest trace of the acetylene hydrocarbons, it was concluded that hydrocarbons of the acetylene series must be absent. Thinking it possible that the gas might be allene (dimethylenemethane, $CH_2: C: CH_2$) which does not give a precipitate with ammoniacal solutions of silver nitrate or cuprous chloride, but which does give a precipitate when passed into a solution of mercuric chloride, the gas was passed several times back and forth through an aqueous solution of mercuric chloride contained in the small U-tube. No precipitate was formed, however, and it was hence concluded that allene was not present in the gas. In order to determine whether any volatile sulphur compounds, formed by the decomposition and reduction of the sulphuric acid, were present, about half a liter of the gas was burned from a platinum-tipped burner in a Drehschmidt's apparatus used for estimating sulphur in coal-gas. No sulphuric acid could be detected in the solutions in the absorption-bottles, and hence it was concluded that no sulphur compounds were present in the gas. The absorption of the gas by fuming sulphuric acid and the fact that it decolorized bromine water, though to be sure slowly, seemed to point to the presence of hydrocarbons of the ethylene series. It was noted, however, that the longer the gas remained in contact with the fuming sulphuric acid the more it was absorbed, while if it were simply passed into the sulphuric acid pipette and then back again into the burette the amount

[1] Bull. Soc. Chim. (Paris) 1888, **1**, 335.

absorbed was much less. With bromine-water, too, the gas did not act like an alkylene, for though it decolorized bromine-water, it did so very slowly, and after being in contact with an excess of bromine-water the absorption ceased after a time, though there was much gas left. Explosion-analyses were now made with the gas, using Hempel's explosion-pipette.[1] The results follow:

	I.	II.
Volume of gas taken,	5.9 cc.	6.1 cc.
Volume of gas + oxygen,	29.5	30.0
Volume of gas + oxygen + air,	96.4	96.4
Volume after explosion,	79.3	78.7
Contraction,	17.1	17.7
Volume after absorption with potash,	61.1	59.9
Carbon dioxide,	18.2	18.8
Volume after absorption with phosphorus,	54.4	54.5
Oxygen used,	30.2	31.7
Reduced to unit volume of gas :		
Contraction,	2.89	2.90
Carbon dioxide,	3.08	3.08
Oxygen used,	5.12	5.20

The following table gives the theoretical figures for each of the gases named below :

	Propane.	Propylene.	Allylene.
Contraction,	3.00	2.50	2.00 vols.
Carbon dioxide,	3.00	3.00	3.00
Oxygen used,	5.00	4.50	4.00

It will be seen from this table that the results of the explosion-analyses on the gas agree better with those required for propane than with any of the others. Propane was now made, first by the method of Schorlemmer,[2] by the action of zinc and dilute sulphuric acid on isopropyl iodide, but it was found that the gas made in this way contained a considerable quantity of hydrogen. It was accordingly made from an alcoholic solution of isopropyl iodide by the action of the zinc-copper couple, according to the method of Gladstone and Tribe[3] for methane. The isopropyl iodide used was made from glycerin, according to the directions of Markownikow.[4] It boiled at 89°–90° C. at 740 mm. barometric pressure,

[1] Hempel's Gas Analysis, trans. by Dennis (Macmillan), page 102.
[2] Ann. Chem. (Liebig) **150**, 209.   [3] J. Chem. Soc. 1884, 154.
[4] Ann. Chem. (Liebig) **138**, 364.

the mercury column of the short Anschütz thermometer being entirely surrounded by the vapor of the boiling liquid. In order to determine whether it contained any allyl iodide or not, some of the isopropyl iodide in alcoholic solution was shaken up with some mercury and allowed to stand for some time. No trace of the mercury-allyl iodide (HgC_3H_5I) was formed, and hence it was concluded that the isopropyl iodide contained no allyl iodide. The propane made from this isopropyl iodide was a colorless gas, with a disagreeable odor, slightly soluble in water, more readily soluble in alcohol. It burned with a luminous, smoky flame, and in general exhibited the properties of the gas obtained by the action of concentrated sulphuric acid on acetone. Analyses of this gas, using the explosion-pipette of Hempel, gave the following results:

	I.	II.
Volume of gas taken,	4.9 cc.	6.0 cc.
Volume of gas + oxygen,	24.2	23.8
Volume of gas + oxygen + air,	98.9	99.1
Volume of gas after explosion,	83.4	80.6
Contraction,	15.5	18.5
Vol. of gas after absorption with potash,	68.4	62.6
Carbon dioxide,	15.0	18.0
Vol. of gas after absorption with phosphorus,	59.4	60.4
Oxygen used,	25.2	30.4
Reducing to unit volume :		
Contraction,	3.16	3.08
Carbon dioxide,	3.06	3.00
Oxygen used,	5.15	5.11

For pure propane the figures should be : contraction, 3.00 ; carbon dioxide, 3.00 ; oxygen used, 5.00.

This propane made from isopropyl iodide was absorbed when passed into fuming sulphuric acid, the amount of absorption depending on the length of time the gas remained in contact with the acid. After allowing the gas to remain in contact with fuming sulphuric acid in a Hempel sulphuric-acid pipette for 15 days, it was found that over 50 per cent. of the gas was absorbed, the sulphuric acid becoming first yellow, and, finally, deep red in color. That propane, a member of the marsh-gas series of hydrocarbons, should be absorbed by fuming sulphuric acid—a reagent that is in general use in gas-analysis to absorb unsaturated hydrocarbons—

seemed very remarkable. The experiment was repeated, however, again and again, and always with the same result. Indeed, the amount of absorption seemed to be limited only by the length of time the gas and sulphuric acid remained in contact. 20 cc. of the gas left in contact with fuming sulphuric acid for two months left only 6 cc. of gas, and the absorption was still going on. Meyer and Jacobson in their Lehrbuch der Organischen Chemie (page 444) state: "Man benutzt daher die rauchende Schwefelsäure in der Gasanalyse—z. B. bei der Analyse des Leuchtgases—um die Alkylene zu absorbiren und durch die infolgedessen eintretende Volumverminderung des Gases den Gehalt an Alkylenen festzustellen. Wasserstoff, *Sumpfgas und seine Homologen,* Kohlenoxyd, etc., werden von der rauchenden Schwefelsäure nicht absorbirt, wohl aber ausser den Alkylenen auch das Acetylen und seine Homologen und die aromatischen Kohlenwasserstoffe (Benzol, etc.)." From the results obtained above with propane it is evident that fuming sulphuric acid cannot be used as an absorbent for the unsaturated hydrocarbons if propane be present. Nowhere in the literature could any statement be found regarding the absorption of propane by fuming sulphuric acid. However, an article by Frankland was found, entitled "The Illuminating Power of Hydrocarbons,"[1] in which the Gladstone and Tribe method for making ethane and propane is described. In this article Frankland states that the propane made by the action of granulated zinc on an alcoholic solution of isopropyl iodide, was found to contain 2 *per cent. of gas soluble in fuming sulphuric acid*, even after the gas had been passed through an alcoholic soda solution, bromine and water, a strong solution of caustic soda, and an eprouvette filled with lime. And though he passed the gas again through the same series of reagents, omitting only the alcoholic solution of caustic soda, he states that *the amount of gas soluble in fuming sulphuric acid was not very materially diminished.* Frankland probably passed the gas from the burette into the sulphuric-acid pipette, and then ran it back again at once into the burette. Had he allowed the propane to remain in contact with the fuming sulphuric acid for any length of time, the absorption would have been still greater.[2] In its action towards bromine-water the pro-

[1] J. Chem. Soc. **47** (1885), 235.
[2] An investigation on the absorption of ethane, propane and butane by the various reagents used in gas analysis, is now in progress in this laboratory.

pane made from isopropyl iodide was found to conduct itself in a manner similar to that exhibited by the gas from the action of sulphuric acid on acetone. When passed back and forth through a small bulbed U-tube containing bromine-water, it slowly decolorized the bromine-water. The action on the bromine-water was slower than that of the gas from acetone and sulphuric acid, but in general it was the same. When the gas was passed into a pipette containing bromine-water and the pipette was shaken with the propane, about 30 per cent. absorption took place. Some of this absorption was, however, undoubtedly due to the solvent action of the water on the gas.

From the results of the analyses, as well as from the general agreement of the properties and chemical conduct of the two gases, we must conclude that the gas obtained from the action of sulphuric acid on acetone is propane.

Crude Mesitylene.—This product, which formed the upper layer in the receiver, was obtained in the form of a light yellow, mobile oil saturated with sulphur dioxide. To remove this and any other acids which might be present, the crude mesitylene was shaken with caustic soda solution several times and then washed with water. It was then dried in the usual manner with fused calcium chloride. Thus purified, it still had a disagreeable odor, somewhat like that of the mercaptans. With mercury salts it was found to give the reaction for the mercaptans, and when heated with sodium, the product resulting, on treatment with water, gave the reaction with sodium nitroprusside for sodium sulphide. In order to remove these sulphur compounds, the crude mesitylene, freed from acids and from any soluble compounds by the above treatment, was heated to boiling for several hours with thin slices of metallic sodium, in a round-bottom flask connected with a return-condenser. The crude mesitylene became dark colored, and when the contents of the flask cooled, a dark brown gelatinous mass remained suspended in the liquid. It was found impossible to separate the liquid from this gelatinous mass either by filtration or by decantation, since it clogged the filter-paper and remained suspended in the liquid even after long standing. Working with a small quantity of the material, it was found that by diluting with ether the gelatinous mass subsided quickly and the ethereal solution could then be readily decanted off. Two volumes of absolute ether were accordingly added to the whole of the material and the

two liquids well shaken together for some time. The ethereal solution was decanted off after the gelatinous mass had settled. The material left in the flask was then treated several times with ether to extract all the oil, and these portions were added to the first extract. The ether was then distilled off and the treatment with sodium repeated until it ceased to act on the oil. The oil had now lost its disagreeable odor and had only a pale straw-yellow color. It was subjected to fractional distillation in a distilling-flask having a short column of beads in the neck. This flask was placed in a copper air-bath which was heated by a burner. By means of this air-bath and column of beads the temperature could easily be regulated, and a better separation of the oil into its constituents was hence effected by their use. Fractions were taken off at intervals of ten degrees, beginning with the fraction from 160°–170°. About 60 per cent. of the crude mesitylene came over at this point. This was found to consist almost entirely of mesitylene. After careful refractioning, over half a kilogram of pure mesitylene boiling at 164° at 745 mm. barometric pressure, was obtained from the 1.05 kilograms of crude mesitylene. This corresponds to over 11.5 per cent. of the theoretical yield.

After several weeks spent in fractioning the higher-boiling products from the crude mesitylene, fractions were obtained which boiled constantly at 183°–185° and 195°–197° C. The product boiling at 183°–185° was a light, colorless, mobile liquid with quite a marked aromatic odor. Its specific gravity at 0° compared with water at 4° C. was 0.8865. Combustion analyses of the substance gave the following results :

	I.	II.	III.	Average.
Carbon,	81.40	81.66	81.66	81.57
Hydrogen,	10.86	10.90	10.74	10.83
Oxygen (by difference),	7.74	7.44	7.60	7.60

For the formula $C_{14}H_{22}O$ the results would be : carbon, 81.55 ; hydrogen, 10.67 ; oxygen, 7.78. It will be seen from a comparison of these figures with the average of the results obtained on analysis, that the latter correspond closely with the formula $C_{14}H_{22}O$.

The vapor-density was determined according to the method of Victor Meyer. The following are the results :

	I.	II.
Weight of substance taken,	0.1725	0.0938
Air displaced,	23 cc.	11.9 cc.
Temperature,	24.5°	26°
Barometer,	746 mm.	747 mm.

	Found.		Calculated for $C_{14}H_{22}O$.
	I.	II.	
Vapor-density,	6.64	7.05	7.16

The formula of the substance boiling at 183°–185° C. is therefore $C_{14}H_{22}O$. Nothing further could be learned regarding this substance, all of it having been used up in the experiments described.

The product boiling at 195° to 197° C. was a colorless liquid with an odor similar to that of mesitylene, but much more marked. It was insoluble in water, but readily soluble in alcohol and in ether. It remained liquid at a temperature of —40° C., although kept at this temperature for several hours. Its specific gravity at 0° compared with water at 4° C. was found to be 0.8961. About 25 grams of this substance were obtained. Combustion-analyses gave the following results:

I. 0.1421 gram gave 0.4693 gram CO_2 and 0.1382 gram H_2O.
II. 0.2490 gram gave 0.8184 gram CO_2 and 0.2403 gram H_2O.

	Found.		Calculated for $C_{10}H_{14}$.
	I.	II.	
Carbon	90.01	89.63	89.56
Hydrogen	10.80	10.72	10.44

The empirical formula appears therefore to be $C_{10}H_{14}$. This agrees with the statements of Fittig and Holtmeyer. A determination of the vapor-density of the substance by the Victor Meyer method gave the following results:

	I.	II.
Weight of substance taken,	0.1352	0.0986
Air displaced,	23.1 cc.	17.5 cc.
Temperature,	16°	17.5°
Barometer,	736.7 mm.	736.4 mm.

	Found.		Calculated for $C_{10}H_{14}$.
	I.	II.	
Vapor-density,	5.04	4.88	4.64

The bromine product was made by adding directly but cautiously four equivalents of bromine to one of the substance contained in a small flask, the flask being cooled by ice-water. A

very violent reaction took place, fumes of hydrobromic acid were abundantly given off and there remained in the flask a solid white material. This was washed with water to free it from bromine and hydrobromic acid, dried and recrystallized from hot alcohol. It was found rather difficult to get the product to melt sharply. This was probably due to the presence of another bromine product with a higher melting-point. After five or six crystallizations from hot alcohol, crystals were obtained which melted sharply at 198° C.

This bromine substitution-product was difficultly soluble in cold alcohol, more readily in hot, and insoluble in water. It crystallizes from hot alcohol in long, glistening white needles which cling together in the form of a matted mass. A determination of bromine in the substitution-product by the Carius method gave the following results:

0.1136 gram gave 0.1462 gram AgBr.

	Found.	Calculated for $C_{10}H_{12}Br_2$.
Br	54.76	54.79

These results show that the product is a dibrom substitution-product of the hydrocarbon $C_{10}H_{14}$. They are in accord with the statements of Fittig and Holtmeyer. A dinitro derivative was made by adding the hydrocarbon to a mixture of fuming nitric and sulphuric acids. A light yellow solid resulted from this reaction. This was subjected to distillation in steam to remove other products, separated from the water, and after three crystallizations from alcohol was found to melt sharply at 157°. Unfortunately but a very small quantity of this substance was obtained and no analyses could be made of it. The product was of a light yellow color, crystallized from alcohol in fine needles, and sublimed quite readily when heated. It was soluble in hot alcohol, less so in cold, and imparted a marked odor of musk to anything with which it came into contact. This odor was especially noticeable when only a very minute quantity was present. The crystals themselves seemed to possess the odor only to a slight degree. This odor of musk was very tenacious, vessels which contained some of the substance three years ago still retaining the odor.

Of the hydrocarbons known having the formula $C_{10}H_{14}$ none agrees with the hydrocarbon under discussion so well as isodurene, unsymmetrical tetramethylbenzene. The following table shows how closely they agree:

	Isodurene.	Hydrocarbon $C_{10}H_{14}$.
Boiling-point,	$195°-197°$ (corr.)[1]	$195°-197°$ (corr.)
Melting-point of dibrom derivative,	$199°$[2]	$198°$
Melting-point of dinitro derivative,	$156°$	$157°$

Isodurene does not solidify at $-20°$ C. The hydrocarbon $C_{10}H_{14}$ could not be solidified at $-40°$ C. Some isodurene was then made according to the method of Jacobsen[3] by the action of methyl chloride on mesitylene in the presence of aluminium chloride. This, after careful fractional distillation, was found to agree in all respects with the hydrocarbon $C_{10}H_{14}$ obtained from the crude mesitylene. It had the same boiling-point and specific gravity, the same odor, and yielded with bromine a dibrom-product melting at $198°$ and with nitric and sulphuric acid a dinitro-product melting at $157°$. In order to determine absolutely whether this hydrocarbon $C_{10}H_{14}$ was identical with isodurene or not, both hydrocarbons were oxidized with a solution of potassium permanganate.[4] Both gave mellophanic acid, tetracarboxylbenzene, as the final product of the oxidation.

From these results it was concluded that the hydrocarbon was isodurene, notwithstanding Jacobsen's statements to the contrary. It was also concluded that the nitro-product obtained by Fittig and Holtmeyer from this hydrocarbon was the dinitro-product, and not the trinitro-product as stated by these authors. It will be seen also from the above results that *pure* acetone when decomposed with concentrated sulphuric acid according to the method described, gives 11.5 *per cent. of the theoretical yield of mesitylene, and that higher-boiling products than mesitylene are formed in the reaction.* As these results are not in accord with the statement of Victor Meyer based on Bielefeldt's work, that "mesitylene is not formed from pure acetone, but only from the commercial acetone by condensation with concentrated sulphuric acid," and as they do not agree with Jacobsen's assertion that "if pure acetone be used in the reaction, no higher-boiling products than mesitylene are formed," experiments were undertaken, using chemically pure acetone in the reaction. This acetone was made from the sodium bisulphite compound, and was found to boil constantly at $54.8°-55.2°$ at 727 mm. barometric pressure, using an Anschütz thermometer, the mercury column being entirely sur-

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[1] Jacobsen gives $195°$ (corr.).   [2] Jacobsen (Ber. d. chem. Ges. **15**, 1853) gives $209°$.
[3] *Ibid*. **14**, 2629.   [4] *Ibid*. **17**, 2517.

rounded by the vapor of the boiling liquid. Over a kilogram of this acetone was decomposed with concentrated sulphuric acid according to the method described above. *The products of the reaction were absolutely identical with those obtained in the first case*, so that it can be positively asserted that the *purest* acetone *does* yield mesitylene when treated with concentrated sulphuric acid and distilled, indeed this method can be recommended as the best known at present for the preparation of mesitylene. It may also be stated that higher-boiling products than mesitylene are formed when the purest acetone is used in the reaction.

Attention should perhaps be called to the fact that Bielefeldt's and Jacobsen's results were obtained by using Fittig's method for the preparation of mesitylene, while the results recorded in this paper were obtained by using a modification of Varenne's method.

The Tar.—The mass remaining in the flask after the distillation in steam was poured out into a porcelain dish and allowed to cool. The spent acid was then poured off, and the black tarry mass remaining was washed several times with water and sodium carbonate solution to remove all the sulphuric acid. It was then washed again with water and dried at 100°. When cold it could easily be broken and handled, and was found to resemble the pitch obtained in the distillation of coal-tar. This tar was then subjected to distillation in an iron retort. The distillate consisted of a brown, thick oil with a disagreeable odor, while the mass left in the retort resembled coke. The distillate was redistilled in a vacuum. It boiled from 100° to 300° at 6 cm. pressure. The distillate was then boiled with sodium for several hours to remove sulphur compounds according to the method given above for the purification of the crude mesitylene; it was then separated from the sodium compounds, redistilled, and again treated with sodium. The oil had now lost its disagreeable odor and gave no reaction for sulphur compounds. The product thus purified was now subjected to fractional distillation, using the apparatus described as used to fractionate the crude mesitylene. The fractions were taken off at intervals of ten degrees from 220° to 290°. The fraction boiling at 270° to 280° was by far the largest of all. The fractions boiling over 220°, obtained from the crude mesitylene and having the corresponding boiling-points, were now added to the proper fractions obtained from the tar, and the combined material was subjected to fractional distillation for several

weeks. A compound boiling at 280°–282° was finally separated. This was quite a viscous liquid, with a yellow color and very little odor. Combustion-analyses gave the following results:

	Found.		Calculated for
	I.	II.	$(C_3H_4)_5$.
Carbon	89.85	89.80	89.99
Hydrogen	10.34	10.44	10.00

From the results it will be seen that the analyses correspond closely with the formula $(C_3H_4)_5$. Several attempts were made to determine the vapor-density of this hydrocarbon by the Victor Meyer method as well as by the Hofmann method, but without success, owing to the fact that the substance was changed in some way even when heated to the boiling-point of aniline. The molecular weight of this hydrocarbon was finally obtained by determining the freezing-point of the solution in benzene, using Beckman's method and apparatus. The following results were obtained:[1]

Weight of solvent used, 12.88 grams.

Weight Substance.	Per cent. Solution.	Depression.	Molecular Weight.
0.2049	1.5908	0.387	201
0.4055	3.1483	0.762	202
0.7644	5.9348	1.399	208
	Required for $(C_3H_4)_5$,		200

The formula $(C_3H_4)_5$ or $C_{15}H_{20}$ therefore represents the composition of the molecule of this hydrocarbon.

With bromine this hydrocarbon formed a bromine substitution-product which was a heavy oil. Owing to the small quantity of this hydrocarbon obtained, further study of it and its derivatives was impossible. The formation of this product, a polymer of allylene, C_3H_4, seems to indicate that allylene is really formed in some stage of the condensation of acetone to mesitylene, as was first conjectured by Hofmann and afterwards by Fittig.

The Aqueous Layer.—This product is the aqueous portion of the distillate collected in the receiver. It smells strongly of sulphur dioxide. When distilled it gave a small quantity of liquid boiling below 100°, but the larger portion boiled constantly at 100°. The fraction boiling below 100° was refractioned, and then the lower-boiling portion treated with potassium

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[1] These determinations were kindly made for the authors by Dr. John White, of this laboratory.

carbonate. A volatile liquid was thus separated which boiled at 56°–58° and was identified as acetone. The product boiling at 100° was neutralized with sodium carbonate and distilled. The first portions of the distillate came over quite milky and had a strong peppermint-like odor. The distillate was extracted with ether, and after having been separated from the water and dried over calcium chloride the ether was distilled off. An oil boiling at 130° was obtained which was shown to be mesityl oxide. The solution of sodium salts remaining in the flask was evaporated to dryness on the steam-bath and finally heated in an air-bath to 140° C. The thoroughly dried mass was then treated with ethyl-sulphuric acid (made by mixing 1 part alcohol and 2 parts concentrated sulphuric acid) and distilled. The distillate was separated from the water, washed with soda solution, dried with calcium chloride, and again distilled. It was found to boil constantly at 76° (barometric pressure, 745 mm.) and was identified as ethyl acetate by many reactions. The only volatile organic acid present in the aqueous layer was thus shown to be acetic acid. Had other volatile organic acids been present, a mixture of the ethyl salts of these acids would have been formed, and they could have been separated from each other by fractional distillation. This result agrees with the statement of Plantamour,[1] who says that the "watery liquid formed in the preparation of mesitylene contains sulphurous and acetic acids which may be separated by baryta."

Spent Sulphuric Acid.—This is the liquid which, on cooling, separated out from the tar produced in the formation of mesitylene. The dark liquid was poured into ice-water, with constant stirring to prevent rise of temperature. The resulting liquid was neutralized with precipitated chalk, filtered, the filtrate boiled with bone-black to decolorize it, and then evaporated to dryness on the steam-bath. An unpleasant odor resembling that of the geranium (phoron) was noticeable during the boiling of the filtrate with bone-black. A very small residue of a calcium salt which solidified in warty concretions, and which was probably a calcium sulphonate, was left after the evaporation to dryness. It is evident from the very small amount of salt formed in this experiment that all sulphonic acids and ethereal salts of sulphuric acid which might have been formed are decomposed by the subsequent heating with sulphuric acid and distillation in steam.

[1] Gmelin's Handbook of Chemistry, Watts' translation, Vol. IX, p. 9.

SUMMARY.

The results of this work on the products of the condensation of pure acetone with concentrated sulphuric acid may be briefly summed up as follows :

1. Mesitylene is formed in largest quantity, over 11.5 per cent. of the theoretical yield having been obtained. The method can therefore be recommended as the best we have at present for the preparation of this hydrocarbon.

2. A not inconsiderable quantity of the hydrocarbon isodurene (unsymmetrical tetramethylbenzene) is formed at the same time with the mesitylene.

3. A compound boiling at 185° to 187° and having the formula $C_{14}H_{22}O$ is a constant product of this reaction.

4. A hydrocarbon boiling at 280°–282° and having the formula $(C_3H_4)_5$ can be isolated from the tarry products.

5. Propane is formed in small quantity in this reaction.

6. Besides the five products above-named, sulphur dioxide, acetic acid, mesityl oxide, phoron and sulphur compounds are produced.

Regarding the method by which mesitylene is formed from acetone, the authors are of the opinion that the acetone first unites with the sulphuric acid, forming an addition-product exactly as it does with hydrocyanic acid. This union of the acetone and sulphuric acid may be represented as follows : ·

$$\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\!=\!O + \genfrac{}{}{0pt}{}{HO}{HO}\!>\!SO_2 = \underset{\underset{\displaystyle CH_2H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\!<\genfrac{}{}{0pt}{}{OH}{O}\genfrac{}{}{0pt}{}{}{HO}\!>\!SO_2.$$
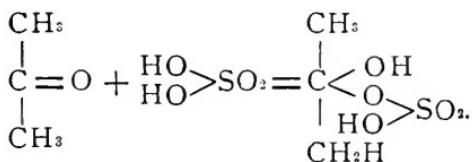
This addition-product then loses water,

$$\underset{\underset{\displaystyle CH_2H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\!<\!\genfrac{}{}{0pt}{}{OH}{O}\genfrac{}{}{0pt}{}{}{HO}\!>\!SO_2 = \underset{\underset{\displaystyle CH_2}{||}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\!-\!\genfrac{}{}{0pt}{}{O}{HO}\!>\!SO_2 + H_2O,$$
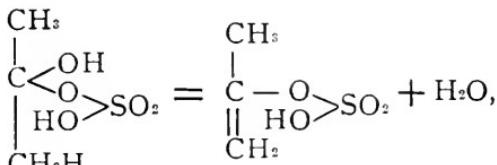
yielding the acid sulphate of isopropenyl alcohol, $CH_3C(OH)\!=\!CH_2$. This isopropenyl sulphuric acid with water yields isopropenyl alcohol and sulphuric acid thus :

$$\begin{matrix} CH_3 \\ | \\ C-O \\ \| \ HO \end{matrix} \Big\rangle SO_2 + HHO = \begin{matrix} CH_3 \\ | \\ C.OH \\ \| \\ CH_2 \end{matrix} + H_2SO_4 \, ;$$
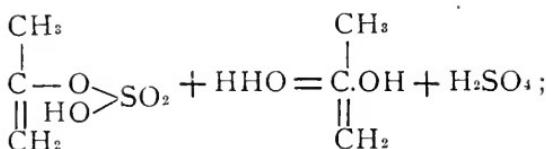
the isopropenyl alcohol forming at once acetone, as it is unstable in the free condition,

$$\begin{matrix} CH_3 \\ | \\ C.OH \\ \| \\ CH_2 \end{matrix} = \begin{matrix} CH_3 \\ | \\ C=O \\ | \\ CH_3. \end{matrix}$$
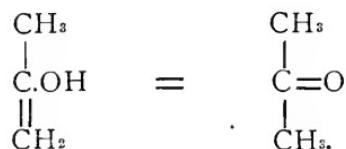
Heated with concentrated sulphuric acid, isopropenyl acid sulphate would yield allylene and sulphuric acid thus:

$$\begin{matrix} CH_3 \\ | \\ C-O \\ \| \ HO \end{matrix} \Big\rangle SO_2 = \begin{matrix} CH_3 \\ | \\ C \\ \| | \\ CH \end{matrix} + H_2SO_4.$$
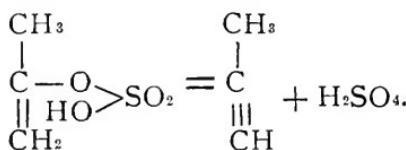
Three molecules of this allylene would then condense in the presence of the strong sulphuric acid and mesitylene would result:

$$\begin{matrix} CH_3 \\ | \\ C \\ \nearrow \\ HC \\ CH_3C \quad CH \\ \| | \quad \| | \\ HC \quad C.CH_3. \end{matrix} \quad . = \quad \begin{matrix} CH_3 \\ C \\ \diagup \diagdown \\ HC \quad CH \\ | \quad \| \\ H_3CC \quad CCH_3 \\ \diagdown C \diagup \\ H \end{matrix}$$
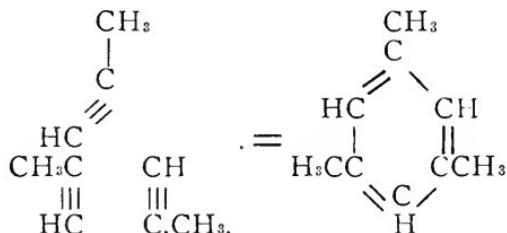
The formation of mesitylene, then, from acetone resembles very closely that of ethylene from ethyl alcohol by the action of sulphuric acid. In the case of the ethyl alcohol, ethyl-sulphuric acid is first formed; this in presence of water gives, as is well known, ethyl alcohol and sulphuric acid, but if heated with more sulphuric acid it yields ethylene, which, however, is not polymerized by sulphuric acid. The equations representing these reactions are as follows:

$$\begin{matrix} CH_3 \\ | \\ H_2C.OH \end{matrix} + \begin{matrix} HO \\ HO \end{matrix} \Big\rangle SO_2 = \begin{matrix} CH_3 \\ | \\ H_2C-O \\ HO \end{matrix} \Big\rangle SO_2 + H_2O$$

Ethyl sulphuric acid.

$$CH_3 \qquad\qquad CH_3$$
$$\underset{HO}{|}\;H_2C-\underset{HO}{O}{>}SO_2 + HHO = \underset{\text{Ethyl alcohol.}}{H_2C.OH} + H_2SO_4$$

$$CH_3 \qquad\qquad CH_2$$
$$\underset{HO}{|}\;H_2C-\underset{HO}{O}{>}SO_2 = \underset{\text{Ethylene.}}{\underset{CH_2}{||}} + H_2SO_4{}^1$$
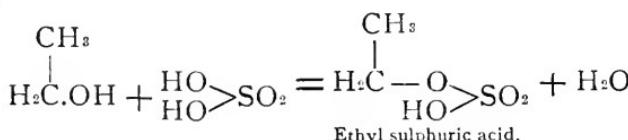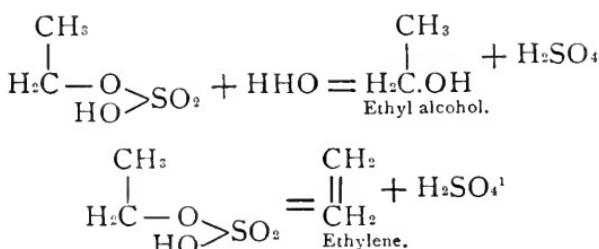
In support of this view of the formation of mesitylene from acetone, it may be said that when acetone and sulphuric acid are mixed, so much heat is evolved that it is necessary to cool with ice-water the flask in which the two liquids are mixed. The mixture is thick and oily, and has lost the odor of acetone entirely. If this mixture of acetone and sulphuric acid (30 grams acetone to 50 of acid) be treated with a liter of water and distilled, almost all the acetone used may be recovered. The product formed by the action of sulphuric acid on acetone, and which the authors believe to be isopropenyl-sulphuric acid, is then decomposed very readily by water into acetone and sulphuric acid. Many attempts were made to prepare salts of this acid, but all failed owing to the fact that in the presence of water the acid decomposes into its constituents.

Both Kane[2] and Hlasiwetz[3] claim to have made salts of the acid obtained by the action of sulphuric acid on acetone. They both speak of the instability of this acid and say that it could only be investigated in its salts. Analyses of the calcium salt of this acid are given by Kane and also by Hlasiwetz, but as the acetone used by them was impure and the calcium salt itself was not purified by recrystallization, the analyses are practically of no value. Kane gives to the acid the formula $C_3H_5HSO_4$, while Hlasiwetz claims that it is to be represented by the formula $C_3H_5HSO_3$. The analyses of the calcium salt do not agree very well with each other nor with either formula.

It is very probable that this same isopropenyl acid sulphate is formed when allylene dissolves in concentrated sulphuric acid. Fittig found that if this solution be diluted with water and distilled, acetone is formed, while if it be diluted with but little water and distilled, mesitylene results. These reactions may be represented as follows:

[1] Meyer and Jacobson: Organ. Chemie **1**, 438.
[2] J. prakt. Chem. **15**, 144. Ann. der Phys. Pogg. **44**, 179. [3] *Ibid.* **69**, 369.

$$\begin{array}{c} CH_3 \\ | \\ C \\ ||| \\ CH \end{array} + \dfrac{HO}{HO}{>}SO_2 = \begin{array}{c} CH_3 \\ | \\ C- \\ || \\ CH_2 \end{array} \dfrac{O}{HO}{>}SO_2,$$

Isopropenyl acid sulphate.

$$\begin{array}{c} CH_3 \\ | \\ C- \\ || \\ CH_2 \end{array} \dfrac{O}{HO}{>}SO_2 + H_2O = \begin{array}{c} CH_3 \\ | \\ C.OH \\ || \\ CH_2 \end{array} = \begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + H_2SO_4,$$

Isopropenyl alcohol.

$$\begin{array}{c} CH_3 \\ | \\ C- \\ || \\ CH_2 \end{array} \dfrac{O}{HO}{>}SO_2 = \begin{array}{c} CH_3 \\ | \\ C \\ ||| \\ CH \end{array} + H_2SO_4,$$
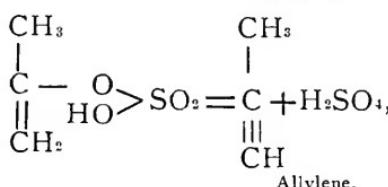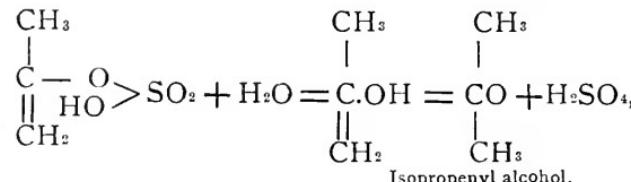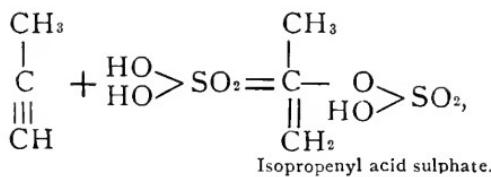
Allylene.

three molecules of the allylene thus formed uniting at once and yielding mesitylene. The reactions represented above are strictly analogous to the reactions by which ethylene is converted into alcohol and back again into ethylene : ethyl-sulphuric acid is first formed, and this with water yields ethyl alcohol and sulphuric acid, but when heated with sulphuric acid it gives ethylene and sulphuric acid, thus :

$$\begin{array}{c} CH_2 \\ || \\ CH_2 \end{array} + \dfrac{HO}{HO}{>}SO_2 = \begin{array}{c} CH_3 \\ | \\ H_2C.O.SO_2H, \end{array}$$

Ethyl-sulphuric acid.

$$\begin{array}{c} CH_3 \\ | \\ H_2C.O.SO_2H \end{array} + H_2O = \begin{array}{c} CH_3 \\ | \\ CH_2OH \end{array} + H_2SO_4,$$

Ethyl alcohol.

$$\begin{array}{c} CH_3 \\ | \\ H_2C.O.SO_2H \end{array} = \begin{array}{c} CH_2 \\ || \\ CH_2 \end{array} + H_2SO_4.$$

Ethylene.
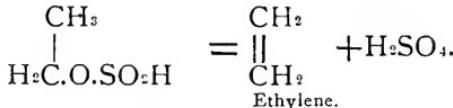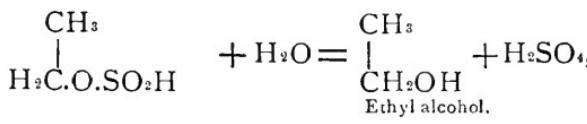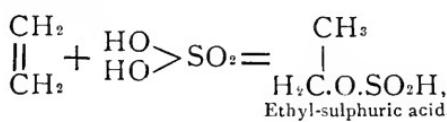
The polymerization of the unsaturated hydrocarbons by sulphuric acid is well known : thus, isobutylene, C_4H_8, forms a di- and tri-isobutylene. According to Butlerow,[1] an addition-product is first formed, thus :

$$(CH_3)_2.C = CH_2 + H_2SO_4 = (CH_3)_2.C{<}{{}^{CH_3}_{SO_4H}}\cdot$$

[1] Ann. Chem. (Liebig) **189**, 65.

This with a second molecule of isobutylene condenses to diisobutylene, sulphuric acid splitting off, thus :

$$(CH_3)_2.C:CH_2+HSO_4.C.(CH_3)_3=(CH_3)_2.C:CH.(CH_3)_3+H_2SO_4$$
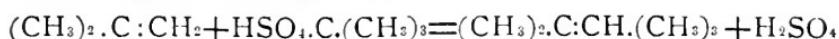
The diisobutylene thus formed then unites with another molecule of the sulphuric-acid addition-product of isobutylene, forming triisobutylene and sulphuric acid.

It is quite likely that the polymerization of allylene by sulphuric acid takes place in a similar manner, an addition-product, isopropenyl acid sulphate, being first formed. This would then unite with another molecule of allylene to form diallylene, sulphuric acid being eliminated, and the diallylene would in the same way form triallylene or mesitylene by uniting with a molecule of isopropenyl acid sulphate. The formation of the product boiling at 280°–282°, having the formula $(C_3H_4)_5$, and which may be called pentallylene, indicates that this view is not altogether improbable.

Acetylene is slowly absorbed by concentrated sulphuric acid, and, if the solution thus formed be distilled with water, acetic and crotonic aldehydes are formed.[1] According to Zeisel,[2] a sulphonic acid is formed here ; but it is quite probable that the reaction is similar to that which takes place when allylene is absorbed by sulphuric acid ; vinyl acid sulphate is probably first formed by direct addition of the acetylene and sulphuric acid, according to the equation :

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + \begin{array}{c} HO \\ HO \end{array}\!\!> SO_2 = \begin{array}{c} CH_2 \\ || \\ HC\!-\!O \\ HO \end{array}\!\!> SO_2.$$

<div align="center">Vinyl acid sulphate.</div>
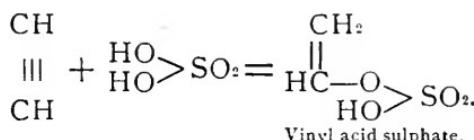
This vinyl acid sulphate with water would then on distillation yield vinyl alcohol and sulphuric acid, the vinyl alcohol at once forming aldehyde, thus :

$$\begin{array}{c} CH_2 \\ || \\ HC\!-\!O \\ HO \end{array}\!\!> SO_2 + H_2O = \begin{array}{c} CH_2 \\ || \\ HC.OH \end{array} = \begin{array}{c} CH_3 \\ | \\ HC = O \end{array} + H_2SO_4 ;$$

<div align="center">Vinyl alcohol. Aldehyde.</div>
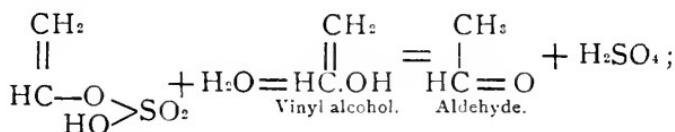
the crotonic aldehyde resulting from the further action of the sulphuric acid on the aldehyde. Vinyl alcohol and its derivatives have been known for some time, but isopropenyl alcohol is not

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[1] Ber. d. chem. Ges. **10**, 637. [2] Ann. Chem. (Liebig) **191**, 372.

known in the free state : it at once yields acetone.[1] It is, however, known in the form of the ethyl ether,[2] which is formed by heating allylene with alcoholic potash to 170°–180°. The reaction is represented thus :

$$CH_3C \equiv CH + HOC_2H_5 = CH_3.C(OC_2H_5): CH_2.$$
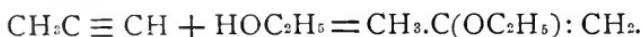
This ether is very readily decomposed by dilute sulphuric acid into acetone and ethyl alcohol.

Concerning the formation of the other products of the reaction between acetone and sulphuric acid nothing further was learned.

The authors of this paper wish to express their thanks to Mr. E. M. Chamot of this University for the analyses of the gas formed in the reaction, as well as of the propane.

PENTOSANS IN PLANTS.

By G. De Chalmot.

Continuing my work[3] of last summer, I investigated the conduct of the pentosans by the germination of seeds. The methods which I used for the detection and quantitative analysis of the pentosans in their different forms are the following :

1st. For the determination of total pentosans I use in principle the method of Tollens and myself. I follow the additional hints given by Flint,[4] making some alterations on account of the small amount of pentosans contained in seeds. I proceed as follows : I distil very slowly (10 cc. in 20 minutes), adding every 20 minutes 10 cc. of hydrochloric acid All the furfurol will be found in the first 100 or 110 cc. of the distillate. After neutralizing as usual, I bring the volume of the liquid to 200 cc. by adding a 19.3 per cent. sodium chloride solution. After precipitating the furfurol I stir for half an hour, following the directions of Flint. As Flint[5] found that furfurol-hydrazon is nearly insoluble in a stronger solution of sodium chloride, I neglect the small amounts which remain

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[1] Meyer and Jacobson: Org. Chem. **1**, 475.   [2] Ber. d. chem. Ges. **21c**, 614.
[3] See this Journal **15**, 21.   [4] Inaug. Diss. (Göttingen) 1892.   [5] *l. c.* p. 20.

in the solution. I further assume that the pentosans yield 50 per cent. of furfurol, which figure renders the calculation easy. When working as described, I got nearly as good results as those obtained by Flint, and found the method more practical if only small amounts of pentosan are present. It requires, though, much watching, as the results can vary greatly if the time of the distillation is not kept within the limits. When larger amounts of pentosans are present, the old way of working seems to me preferable.

2d. For the determination of the pentosans which are insoluble in dilute acids (cellulose-pentosans), I heat 10 grams of substance with 200 cc. of hydrochloric acid (of 1.25 per cent. HCl). I heat the insoluble residue three times more with water, place it on a filter, dry it and distil it with 100 cc. of hydrochloric acid (of 12 per cent. HCl).

3d. To detect the small amounts of soluble pentosans I determine the total amount of carbohydrates and the amount of furfurol obtained by distillation with hydrochloric acid, as described in my former paper.

Last summer I assumed that the largest amount of furfurol which hexoses can yield is 0.2 per cent. As I based this presumption on analyses made with small amounts of cane sugar only, it seemed to me not superfluous to repeat those analyses, taking larger amounts of cane sugar and of sugar of milk.[1] For these determinations I used the colorimetric method.

Cane sugar recrystallized out of dilute alcohol in large crystals: (1.) 5 grams substance taken. The strength of the furfurol solution was $+0.5$ cc., therefore the sugar yielded 0.125 per cent. of furfurol. (2.) 5 grams substance, $+(0.5-1)$ cc. or 0.1375 per cent. of furfurol. Average of two analyses is 0.13 per cent. of furfurol. The percentage obtained with 0.5 gram of cane sugar last summer was 0.04–0.2 per cent. of furfurol.

Sugar of milk recrystallized out of water: (1.) 5 grams substance, $-(2.5-3)$ cc. or 0.042 per cent. of furfurol. (2.) 5 grams substance, $-(2-2.5)$ cc. or 0.047 per cent. of furfurol. Average of two analyses is 0.045 per cent. of furfurol.

Allowing that glucose and galactose yield the same percentage of furfurol, and considering that 5 grams of sugar of milk yield

[1] With regard to the presence of galactans in seeds see Schulze, Steiger and Maxwell: Landw. Vers. St. **39**, 269–329.

2.63 grams of glucose and 2.63 grams of galactose, glucose and galactose each yield 0.043 per cent. of furfurol. Cane sugar yields equal amounts of glucose and of fructose. The percentage of furfurol yielded by fructose can now be calculated, being 2(0.13 × 0.95)—0.043 or nearly 0.2 per cent. The figure 0.2 per cent. for the largest possible amount of furfurol which hexoses can yield, is therefore well chosen.

In all the seeds which I tested I found water-soluble methyl-pentosans which yield methylfurfurol. I had therefore to detect furfurol in a solution in which also methylfurfurol was present. I will communicate in a few words an account of the reactions which proved efficient for the detection of furfurol and of methylfurfurol when present at the same time in an acetic acid solution.[1]

Furfurol, aniline and acetic acid yield a red dye, an acetate of furfur-aniline. Methylfurfurol, aniline and acetic acid yield a yellow dye, probably an acetate of methylfurfur-aniline. The chloride, nitrate and sulphate of furfur-aniline are red.[2] The same salts of methylfurfur-aniline are also red. Furfur-aniline salts cannot be formed unless there is less mineral acid present than is equivalent to the amount of aniline in the solution. The limits in the case of the formation of methylfurfur-aniline salts are the same. Furfur-aniline salts are very unstable. Methylfurfur-aniline salts are much more stable. If small amounts of methylfurfurol are to be detected in the presence of large quantities of furfurol, I treat the acetic acid solution with my aniline reagent (1 per cent. aniline in 95 per cent. alcohol). The dyestuffs are readily formed, but the yellow color is not visible on account of the red being prevalent. I allow the solution to stand exposed to the light until the red color has vanished (one or more days). I add then a drop of hydrochloric acid. If a reddish tinge appears and remains, even after several hours, methylfurfurol has been present. The appearing of a reddish color does not directly prove that methylfurfurol is present, as the chloride of furfur-aniline is a much stronger dye than the acetate is. It is, therefore, possible for the amounts of acetate to be so small as to be invisible. When they are converted into the chloride they become visible, but vanish very soon. To

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[1] The reaction of Maquenne (Compt. Rend. **109**, 571) cannot be used to ascertain the presence of methylfurfurol, when this is strongly diluted.

[2] Hill (Ber. d. chem. Ges. **22**, 607) and Bieler (Inaug. Diss. [Göttingen, 1890] pp. 24) state that methylfurfurol treated with aniline and acetic acid, yields a yellow dye, which gradually changes into orange red, though they do not give an explanation of this change.

use this reaction with perfect certainty requires some experience. To detect small amounts of furfurol in the presence of larger quantities of methylfurfurol is more difficult. The color obtained after adding aniline is yellow, and the red tinge is not visible. If the amount of furfurol present is not too small, it can be made evident by adding to the solution a drop of aniline oil. If this be carefully done the drop sinks to the bottom of the tube, without mixing much with the acid liquid. If furfurol is present a reddish hue can be observed directly above the aniline.[1]

The experiments were made with peas and with corn. Analyses were made of the seeds before germination, and of the different parts of the young plants after germination in darkness. I allowed the seeds to swell in water and then put them into soil. The soil used contained small amounts of pentosans and methyl-pentosans. The roots of the young plants were therefore carefully washed. The matter used for analysis was always finely pulverized and thoroughly mixed. Further details can easily be learned from the figures given below.

Table I.—Peas (*Pisum sativum* L.).

A sample of selected peas weighing each 0.260 gram (0.255–0.265) was used.

a.—*Before the Germination.*

77 peas = 19.0380 grams of dry matter. 1 pea = 0.2474 gram of dry matter.

4.7190 grams of dry matter yielded 0.1784 gram of hydrazon = 3.90 per cent. of total pentosan; 4.5392 grams of dry matter yielded 0.1639 gram of hydrazon = 3.72 per cent. of total pentosan; average = 3.81 per cent. of total pentosan.

9.0740 grams of dry matter yielded, after treatment with acid, 0.0778 gram of hydrazon = 0.88 per cent. of cellulose-pentosan.

b.—*After the Germination from* 19 *November to* 6 *December.*

The average length of the main roots was 12.8 cm., and of the stems 21.4 cm.

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[1] It may be that there are two acetates of furfur-aniline. The one which is formed in the acetic acid solution might be a diacetate. Aniline acting upon this compound might possibly form a monoacetate and aniline hydrochloride. The monoacetate should be a stronger dye than the diacetate. If to a solution of furfur-aniline in acetic acid an excess of aniline is added, the color gets noticeably darker. The study of the acetates is much hindered by reason of their tendency to decompose.

100 plants = 20.40 grams of dry matter.   1 plant = 0.2040 gram of dry matter.

Analyses of plants: 4.8184 grams of dry matter yielded 0.2572 gram of hydrazon = 5.52 per cent. of total pentosan; 4.8146 grams of dry matter yielded 0.2388 gram of hydrazon = 5.12 per cent. of total pentosan; average = 5.32 per cent. of total pentosan.

9.6330 grams of dry matter yielded, after treatment with acid, 0.1262 gram of hydrazon = 1.38 per cent. of cellulose-pentosan.

90 stems = 4.881 grams of dry matter yielded 0.2474 gram of hydrazon.   1 stem contained 0.0028 gram of total pentosan.

90 roots = 3.2970 grams of dry matter yielded 0.1291 gram of hydrazon; 1 root contained 0.0015 gram of total pentosan.

Before the Germination. Gram.	After the Germination. Gram.	Gain or Loss. Gram.
1 seed = .2474 dry matter.	1 plant = .2040 dry matter.	—.0434
1 " = .0094 total pentosan.	1 " = .0109 total pentosan.	+.0015
1 " = .0022 cellulose-pentosan.	1 " = .0028 cellulose-pentosan.	+.0006
	1 stem = .0028 total pentosan.	
	1 root = .0015 " "	
1 " = .0094 total pentosan.	1 seed (by calculation) = .0066 total pentosan.	—.0028

Table II.—Corn (*Zea Mays* L.).

A sample of selected corn was thoroughly mixed.   Of each 5 specimens, 4 were taken for germinating and 1 for analysis.[1]

Average weight of 1 seed for germinating = 0.4776 gram; average weight of 1 seed for analysis = 0.4858 gram.

a.—*Before the Germination.*

4.7706 grams (10 seeds) = 3.9188 grams of dry matter = 82.14 per cent.   1 average seed of 0.4776 gram contained 0.3923 gram of dry matter.

4.2256 grams of dry matter yielded 0.1914 gram of hydrazon = 4.68 per cent. of total pentosan;   4.0946 grams of dry matter yielded 0.1854 gram of hydrazon = 4.62 per cent. of total pentosan;   average = 4.65 per cent. of total pentosan.

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[1] I could not get a sample of corn from which each seed had nearly the same weight, as was the case with the peas.   The weight of the seeds varied a great deal.

8.4511 grams of dry matter yielded, after treatment with acid, 0.0075 gram of hydrazon = 0.09 per cent. of cellulose-pentosan.

b.—*After the Germination from 5–26 December.*

The average length of the stems was 20 cm.

	Grams.		Gram.
344 seeds	= 83.6 dry matter,	1 seed	= 0.2430
344 stems and roots	= 41.8 dry matter,	1 stem and root	= 0.1215
		1 plant	= 0.3645

Analyses of seeds: 4.8335 grams of dry matter yielded 0.2800 gram of hydrazon = 5.98 per cent. of total pentosan; 4.7718 grams of dry matter yielded 0.2685 gram of hydrazon = 5.80 per cent. of total pentosan; average = 5.89 per cent. of total pentosan.

Analyses of stems and roots: 4.8671 grams of dry matter yielded 0.2871 gram of hydrazon = 6.08 per cent. of total pentosan; 4.8700 grams of dry matter yielded 0.2720 gram of hydrazon = 5.76 per cent. of total pentosan; average = 5.92 per cent. of total pentosan.

Before the Germination.	After the Germination.	Gain or Loss.
Gram.	Gram.	Gram.
1 seed = .3923 dry matter.	1 plant = .3645 dry matter.	—.0278
1 " = .0182 total pento-san.	1 seed = .0143 total pento-san.	—.0039
1 " = .0004 cellulose-pentosan.	1 stem + root = .0072 total pentosan.	
1 " = .0182 total pento-san.	1 plant (by calculation) = .0215 total pentosan.	+.0033

The results are chiefly the following: First, the pentosans decrease in the seeds during the germination, and appear again in the stems and roots; they are therefore transferred. Second, the total amount of pentosans increases during the germination.

The amount of cellulose-pentosans also increases, but the difference in the figures obtained from peas is too slight to produce an absolute certainty in this respect.

The amount of cellulose-pentosans in corn being very small, I did not determine it after the germination.

With regard to the first result, it was desirable to trace the soluble pentosans which ought to be present when pentosans are transferred.

When I prepared an extract of the young plants by immersing them in water in the same way as I formerly treated green leaves, I could not trace pentosans in the solution, but methyl-pentosans very distinctly. This tempted me to believe that only methyl-.pentosans were transferred. This being the case, there should be a difference in the melting-points of the hydrazons obtained from seeds before and after germination, as furfurol-hydrazon melts at 98° C., and methylfurfurol-hydrazon is still a liquid at 15° C.[1] In order to test this I dried the hydrazons obtained by four different distillations of corn, in a desiccator, and determined their melting-points. The melting-point of hydrazon from seeds before germination was found to be 87°–88° C., and of hydrazon from seeds belonging to plants of 4 weeks old was found to be 88°–89° C. As the melting-points were nearly the same, the constitution of the hydrazons obtained from seeds before and after germination was also not very different, and the relation between the amounts of pentosans and methyl-pentosans in the seeds was in both cases the same or nearly the same.

I tried once more to trace soluble pentosans, using the pressed-out juice of the young plants, and was successful. In the juice of germinated peas, smaller amounts of methyl-pentosans are contained than in the extract obtained by immersing the germs for a longer time in water.

The juice is much more concentrated than the extract, and on this account the percentage of pentosans in it is larger. The juice from peas of 3½ weeks old yielded a red color with aniline. The color was too brown (presence of methylfurfurol) to be accurately compared with the standard furfurol solution, but there was surely more than 0.00005 gram of furfurol in 1 cc. liquid. The original liquid contained 0.5 per cent. of hexoses, and therefore the hexoses present could not have yielded more than 0.00001 gram of furfurol in 1 cc., and probably they yielded much less.

In a somewhat diluted juice from corn-germs there was still a large amount of methyl-pentosans present. I could distinctly trace furfurol when adding aniline oil as described above. I could not prove that the furfurol was more than what the hexoses (2 per

[1] E. Fischer: Ber. d. chem. Ges. **17**, 574; Hill, *l. c.*

cent.) could yield, but I have no doubt of it, as the amount of furfurol that the hexoses have yielded was probably much less than 0.00004 per cent., and it would not be possible to trace this small amount.

Juice from *Tropæolum* yielded more than 0.0001 per cent. of furfurol. I did not determine the amount of hexoses on account of the small quantity of juice. It was evident, though, that they did not yield so much furfurol.

The fact that pentosans insoluble in water are dissolved in the seeds and transported during the germination is of the highest importance, touching the theory of the formation of pentosans by the assimilating process. I have pointed out in my former article that it is probable that pentosans which are formed by the assimilating process are temporarily precipitated and dissolved when the main assimilation is over.

I have proved now that pentosans when once precipitated can be dissolved and transported again, which gives to the hypothesis a firmer foundation than I was able to give it before.

When discussing this hypothesis I mentioned that it seemed not improbable to me that under the circumstances by which aldehydes can form the polymeric sugars, the reverse could also take place. I was then not acquainted with a recent publication of J. Traeger,[1] who has proved that paraldehyde forms aldehyde again under probably the same circumstances that aldehyde can form paraldehyde. I am gratified that this fact in some degree supports my suggestion.

I found that during the germination the amount of pentosans increases. This result might be due to two different causes: First, the pentosans might be formed out of other substances; second, the pentosans might be absorbed out of the soil in which pentosans are present. In order to know which of these two causes was the true one I allowed peas to germinate into asbestos in which no pentosans are present.

Table III.

40 peas for germinating weighed 8.55 grams, or 1 pea $= 0.2137$ gram.

The sample contained 92.92 per cent. of dry matter, therefore 1 pea before the germination $= 0.1986$ gram of dry matter.

[1] Ber. d. chem. Ges. **25**, 3316.

For analysis, 100 peas = 21.40 grams were used, or 1 pea = 0.2140 gram.

4.5218 grams of dry matter yielded 0.1854 gram of hydrazon = 4.24 per cent. of pentosan; 4.5218 grams of dry matter yielded 0.1886 gram of hydrazon = 4.30 per cent. of pentosan; average = 4.27 per cent. of pentosan.

After germinating from 3–27 of January, the 40 peas weighed when dried 7.910 grams, which included some asbestos that could not be easily removed. A determination of ash showed 35.5 per cent. of it; therefore more than 5 grams had to be used for the determination of pentosan.[1]

6.716 grams of dry matter yielded 0.2908 gram of hydrazon = 4.46 per cent. of pentosan.

Before the Germination.	After the Germination.
1 seed = 0.0085 gram of pentosan.	1 plant = 0.0088 gram of pentosan.

No material gain in pentosans was obtained, and it seems therefore probable that the germs can absorb pentosans out of the soil.

I hope to investigate this matter more thoroughly. Some seeds contain large amounts of pentosans,[2] and it seemed to me not superfluous to examine if also in these seeds the amount of pentosans does not diminish during the germination.

For this examination I used the seeds of *Tropæolum majus.* As the dried-up fruits could not easily be removed, I allowed the seeds to lie in water for some days, after which treatment the fruits could be easily taken away. The germination took place in earth.

Table IV.

209 seeds for germinating = 41.19 grams. 1 seed = 0.1970 gram.

151 seeds for analysis = 29.25 grams. 1 seed = 0.1937 gram.

a.—*Before the Germination.*

151 seeds or 29.25 grams contained 13.0808 grams of dry matter = 44.72 per cent.

1 average seed of 0.1970 gram contained 0.0881 gram of dry matter.

3.9606 grams of dry matter yielded 0.4629 gram of hydrazon

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[1] Flint: *l. c.*   [2] Ber. d. chem. Ges. **25**, 1238.

$=$ 12.08 per cent. of pentosan; 3.9606 grams of dry matter yielded 0.4547 gram of hydrazon $=$ 11.86 per cent. of pentosan; average $=$ 11.97 per cent. of pentosan.

b.—*After the Germination from* 1–15 *January.*

207 plants $=$ 16.61 grams of dry matter. 1 plant $=$ 0.0802 gram. 3.9275 grams of dry matter yielded 0.2289 gram of hydrazon $=$ 6.02 per cent. of pentosan.

Before the Germination.	After the Germination.	Loss.
Gram.	Gram.	Gram.
1 seed $=$ 0.0105 pentosan.	1 plant $=$ 0.0050 pentosan.	—0.0055

These results are striking. The pentosans have diminished by more than one-half.

It remains to be examined whether there are other seeds in which the pentosans decrease so strongly during the germination, and whether the pentosans in *Tropæolum* are the same as those in corn and peas. I hope to be able to furnish a communication on these matters hereafter.

RICHMOND, VA., *February*, 1893.

XXIII.—SOME PRODUCTS OF CASSAVA.[1]

BY E. E. EWELL AND H. W. WILEY.

Some four years ago one of us[2] described a plant which has been grown in Florida for many years under the name of sweet cassava, the botanical name of which is *Jatropha manihot* or Aipi. From the analyses made at that time it was found that the plant was valuable for feeding purposes, being very rich in carbohydrates although rather poor in albuminoids. Lately the subject has been studied to a much greater extent with the object of preparing as large a number of products as possible from the plant, with the determination of their chemical properties and food values.

[1] Read before the Washington Chemical Society, February 9, 1893.
[2] Wiley: Agric. Science, Vol. 2, No. 10, pp. 256 *et seq.*

A large quantity of the root was obtained from Florida, the bark separated from the root and each subjected to analysis with the following results:

| | Peeled root. | | Fiber after removal of starch. | Bark of root. | |
	Fresh.	Dry.	Dry.	Fresh.	Dry.
Moisture,	61.30	..	..	61.30	..
Ether extract,	0.17	0.44	0.30	0.66	1.70
Albuminoids (nitrogen × 6.35),	0.64	1.66	1.02	2.29	5.91
Starch (diastase extract inverted with HCl),	30.98	80.06	64 64	..	..
Fiber,	0.88	2.26	10.68	3.83	9 89
Ash,	0.51	1.31	1.42	2.02	5.23
Undetermined,	5.52	14.27	21.94	29.90	77.27
	100.00	100.00	100.00	100.00	100.00

With the starch in the analysis given above is reckoned also the soluble carbohydrates, consisting almost exclusively of cane sugar, and of which, in an analysis of another portion of the dry substance, as high as 17 per cent. was found. The undetermined portion consists of the digestible fiber and carbohydrates of the pentose series. The pentosans in the fiber were determined by the furfurol process, as modified by Krug, and the amount in the air-dried material was found to be 3.92 per cent., and in the material after the removal of the starch, 5.33 per cent.

The fresh root was found to contain 38.7 per cent. of dry matter, being considerably more than was found in the fresh sample of the previous analysis. Of this 38.7 per cent., 30.98 consisted of starch and soluble carbohydrates.

Experiments were made to determine the yield of air-dry starch which could be obtained from the roots by laboratory work. Two sets of experiments were made. In the first set the roots were pulped on a Pellet rasp used for preparing beet pulp for instantaneous diffusion. 12 kilos of the unpeeled root were rasped in this way and the starch separated by washing through a sieve of bolting cloth. The washings and settlings were collected and dried in the ordinary method of starch manufacture. The yield of pure starch was 3105 grams, equivalent to 25.9 per cent. of the total weight of the root. The starch was almost absolutely pure, containing only a trace of nitrogenous matter. In the second experiments 10 kilos of the root were ground in a pulping machine

used for preparing green fodder for analysis. The pulp was much less fine than that produced by the Pellet rasp. Treated in the same way, the yield of air-dry starch was 2360 grams or 23.6 per cent. One of the striking points in connection with the work is that the residue from the starch, which consisted largely of fiber, as will be seen by reference to the above analysis, contained still a large percentage of starch, showing that by the process employed the whole of the starch was not secured from the pulp. The diameter of the starch granules is a little over .01 mm., being about seven times smaller than the average of potato starch.

The cassava which grows in tropical regions contains a notable percentage of hydrocyanic acid, so great, in fact, that it cannot be used directly as a food. The so-called poisonous cassava is boiled to expel the hydrocyanic acid before being used for feeding purposes. A careful determination was made of the hydrocyanic acid in the fresh root and the amount was found to be .015 per cent. While this shows a considerable quantity of hydrocyanic acid, it is hardly in proportions sufficiently large to be alarming. Nevertheless, any possible danger could be avoided before using the material as a food, by subjecting it to a sufficient heat to expel the hydrocyanic acid. The hydrocyanic acid seems to be distributed throughout the pulp, and particularly in the juices which can be expressed from the pulp. No injurious effect from the hydrocyanic acid has ever been observed in the case of animals fed on cassava in Florida.

The bark of the root was also subjected to analysis, as will be seen by reference to the above table. It contained no starch, the undetermined matter being chiefly digestible fiber and pentosans.

The mineral matters extracted from the soil are distributed as indicated in the table. The amount of ash in the root itself is quite low, showing that the cassava plant does not require a soil very rich in mineral constituents. The amount of mineral matter taken from the soil by 100 kilos of the fresh root is approximately only half a kilo. The albuminous matters are also present in small quantities, being only slightly larger in weight than the ash itself. The plant, therefore, is one which seems particularly suited to feed almost exclusively from the air and water, and hence is one which could be recommended on the sandy soils of Florida as a crop which would require the minimum of fertilization.

Composition of the Ash.

The ash of the peeled root and the bark of the root were subjected to analysis, with the following results:

ANALYSES OF THE ASH OF CASSAVA ROOT.

CONSTITUENTS.	PEELED ROOT.			BARK OF ROOT.		
	A	B.	Mean.	A.	B.	Mean.
Carbon, ...	0.30	0.31	0.31	0.79	0.77	0.78
Silica (soluble in solution of Na₂CO₃), ...	0.97	0.91	0.94	10.53	11.36	10.94
Silica (insoluble in solution of Na₂CO₃), ...	7.15	7.15	7.15	52.99	52.16	52.58
Ferric oxid (Fe₂O₃), ...	0.66	0.66	0.66	2.46	2.44	2.45
Calcium oxid (CaO), ...	10.63	10.64	10.64	6.58	6.65	6.62
Magnesium oxid (MgO), ...	7.36	6.35	7.35	3.31	3.33	3.32
Sodium oxid (Na₂O), ...	1.12	1.28	1.20	0.84	1.05	0.95
Potassium oxid (K₂O), ...	41.72	41.54	41.63	14.73	14.68	14.70
Phosphoric acid (P₂O₅), ...	15.58	15 59	15.58	2.44	2.46	2.45
Sulphuric acid (SO₃), ...	3.67	3.80	3.73	1.71	1.71	1.71
Carbonic acid (CO₂), ...	9.15	9.12	9.14	2.53	2.50	2.51
Chlorine (Cl), ...	2.76	2.75	2.75	1.41	1.42	1.41
Total, ...	101.07	101.10	101.08	100.32	100.53	100.42
Oxygen equivalent to chlorine,	0.62	0.62	0.62	0.31	0.31	0.31
Difference, ...	100.45	100.48	100.46	100.01	100.22	100.11

From the above numbers it is seen that the ash of the peeled root is especially rich in potash, almost one-half of the total weight being composed of this substance. The potash is combined chiefly with carbonic and phosphoric acids. In the ash of the bark, as might be expected, silica is the predominant element, more than half the total weight consisting of this substance.

Assuming a yield of five tons of roots per acre, the weights of the important fertilizing materials removed by such a crop can be readily calculated from the data given.

Since the bark forms approximately 2.2 per cent. of the entire root, the total crop would be made up of the following amounts of bark and peeled root which would contain the amounts of mineral matter given below:

Peeled root,	.	9,780 lbs., containing	49.88 lbs. ash.
Bark of root,	.	220 " "	4 44 " "
		10,000 " "	54.32 " "

The more important mineral matters contained therein are:

	Ash from peeled root, 49.88 lbs. Lbs.	Ash from bark, 4.44 lbs. Lbs.	Total ash from 5 tons, 54.32 lbs. Lbs.
Lime (CaO), ...	5.31	0.29	5.60
Magnesia (MgO), . . .	3.67	0.15	3.82
Potash (K₂O), ...	20.77	0.65	21.42
Phosphoric acid (P₂O₅), .	7.77	0.11	7.88
			38.72

The less valuable mineral plant-foods, that is, those which are of so little note as to require no conservation or addition, amount to 17.60 lbs. per acre.

Quite a number of preparations was made from the starch of the root, and among them may be mentioned: First, tapioca; the first portions of starch washed out, especially, produce an excellent article of tapioca when moistened in the usual way. Second, glucose; both the fresh root and the extracted root yield full theoretical amounts of glucose, and samples of this article were made by the conversion of the starch both by sulphuric acid and diastase. The samples of glucose made from the starch were exceptionally good, especially when diastase was used; the glucose in this case containing large quantities of maltose. Commercially it would be more profitable to make the glucose directly from the fresh root, in which case the considerable percentage of cane sugar contained by it would be saved, whereas if glucose is made from the starch the cane sugar is previously washed out. On account of the presence of the bark, however, the glucose made from the whole root is not so fine in quality as that made from the pure starch. Third, alcohol; the glucose on fermentation affords the usual quantity of alcohol. Fourth, cane sugar; a beautiful preparation of cane sugar was made from the water used in washing out the starch. The amount of cane sugar, however, is not large enough to warrant its extraction on a commercial scale from the waters used for washing. It is, however, present in sufficient quantity to indicate that in making glucose it is better to use the whole root as indicated above.

The general result of the analytical work is such as to establish the fact that the cassava is a plant of high economic value and worthy of the attention of those interested in the carbohydrate products of the country.

REVIEWS AND REPORTS.

Recent Progress in Physical Chemistry, II.

The Theory of Solutions.

2. *Electrolytic solutions.*—The theory of electrolytic dissociation has recently been outlined in this Journal, **12**, 506; its development since that time includes discoveries of serious importance.

Ostwald has shown[1] how the basicities of acids, especially of the organic acids, may be directly determined from the electrical conductivities of their sodium salts. The conductivity of an aqueous solution of the salt, containing one gram-equivalent sodium in 32 liters, is observed; the increase of conductivity upon extending the dilution to 1024 liters (*i. e.*, halving the concentration five times) is always for salts of monobasic acids very nearly 10 units of conductivity; for those of dibasic acids, 20; of tribasic, 30; of tetrabasic, 40; of pentabasic, 50.

Examples given are:

	Diff.
Monobasic: Butyric acid,	10.2
Dibasic: Malonic acid,	20.6
Tribasic: Pseudo-aconitic acid,	29.6
Tetrabasic: Pyridinetetracarbonic acid,	40.4
Pentabasic: Pyridinepentacarbonic acid,	50.1

This singular regularity is due to the fact that at any given concentration the sodium salts of all acids of the same basicity have practically the same degree of electrolytic dissociation.

To determine the affinity-constants (dissociation-constants) of acids it is necessary to know their maximum molecular conductivities μ_∞, since the percentage dissociation (electrolytic) is given by $\alpha = \mu_v/\mu_\infty$, μ_v being the conductivity at any given finite molecular dilution v. They are found in the following manner[2]: We have $\mu_\infty = u + v$,[3] u and v being the migrating velocities of the positive and negative ions respectively. For strongly dissociated salts (as sodium chloride) μ_∞ can be directly measured. Further, we have the ratio of the concentration decrease at the anode to that at the kathode, upon electrolysis of a salt solution (as of sodium chloride), equal to u/v.[4] Combination of these values yields u and v, the migrating velocities of the sodium and chlorine ions. Subtracting v from μ_∞ for hydrochloric acid, a directly measurable quantity, yields the migrating velocity of the hydro-

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[1] Ztschr. phys. Chem. **2**, 901. [2] Ostwald; Ztschr. phys. Chem. **2**, 840.
[3] F. Kohlrausch: Ann. der Phys. Wied. **6**, 167. [4] Hittorf (1853).

gen ion, and subtracting u from μ_∞ for the sodium salt of any organic acid yields that of the negative ion of the acid. The sum of these values is the required conductivity of the acid at entire dissociation, since $\mu_\infty = u + v$. μ_∞ for any sodium salt has been shown to be $\mu_{1024} + 2.4$, the readily ascertained molecular conductivity of one gram-molecule in 1024 liters, *plus* a small constant. Thus may be accurately determined the maximum conductivities of the acids, which are entirely inaccessible to direct measurement, and are yet necessary for finding the affinity-constants, *i. e.*, the dissociation-constants. From data thus obtained, and the molecular conductivities of the acids themselves, Ostwald and his pupils have determined the affinity-constants[1] of about five hundred organic acids[2] of the most widely varying types. The migrating velocities of the negative ions of different organic acids were found by Ostwald[3] to decrease rapidly with increasing number of atoms in the ion; the influence of additional atoms nearly disappearing, however, by about 12–15 atoms. It appeared further that isomeric ions have equal migrating velocities.

The conductivities of that typical electrolyte hydrochloric acid in solution in various organic solvents—benzene, xylene, hexane, ethyl ether, methyl, ethyl, isobutyl and isoamyl alcohols—have been studied by Klabukoff.[4]

The conductivities were in all cases slight, corresponding to the normal vapor-pressures, freezing-points, etc., of these solutions. The greatest conductivity by far was in the methyl-alcohol solution.

In the light of the theory of electrolytic dissociation, which refers the manifestations of acid character to the action of free hydrogen ions, the following observations of Pelouze and Gore[5] are of some interest: Anhydrous acids, being undissociated, have no free hydrogen ions, and, in fact, blue litmus paper remains blue when placed in concentrated sulphuric, acetic, propionic and valeric acids. It also remains blue in water, but if a paper be transferred from one of the acids to the water both turn red, the aqueous acid solution containing free ions. In nitric acid the litmus is at once reddened, but this acid conducts electrolytically and is hence dissociated.

An application of the theory of electrolytic solutions to physiological investigation has been made by F. A. Hoffmann[6] of Leipsic. A study of the velocity with which albumen is digested by pepsin solution, in the presence of acids, has shown it to depend directly upon the dissociation (affinity) of the acid employed. The digestion-velocities yielded, for hydrochloric, phosphoric, arsenic, citric and lactic acids, the regular order, and approximately the numerical value of the percentage dissociations. Sulphuric acid formed an exception, as it acted directly upon the albumen.

[1] See this Journal **12**, 5.
[2] Ostwald: Ztschr. phys. Chem. **3**, 170. Complete review of the literature in a paper by Walden: *ibid.* **8**, 433.   [3] *Ibid.* **2**, 840.   [4] *Ibid.* **4**, 429 (1889).
[5] See Marsh: Chem. News **61**, 2.   [6] Schmidt's Jahrbücher **233**, 268.

The percentage dissociations of organic acids have been recently determined[1] in the following manner: On titrating alkali into acid solutions, in the presence of red lacmoid, the blue color of the lacmoid salt appears when the concentration of the hydrogen ions of the acid has sufficiently decreased to equal that of the lacmoid. So, the weaker the acid employed the sooner the blue color appears. The percentage dissociations thus obtained are in satisfactory agreement with the values calculated from the inversion-velocities and electrical conductivities.

The affinity-constants of a number of organic acids, dissolved in 50-per cent. alcohol, have been determined by Lellmann and Schliemann[2] by comparison with oxyanthraquinone. It and the acid to be studied were brought together with a base, and the amount of the salt of the reference-acid formed was determined by a photometric method. The relative strength of the acids was found to be not quite the same as in aqueous solution (from Ostwald's conductivity measurements). The relative avidities of different acids, *i. e.*, the ratio of the amounts of their salts formed, are given, and these values are approximately equal to the square roots of the ratios of the corresponding dissociation-constants, as is required by the dissociation theory. Attention has been called to this point by Arrhenius.[3] Further, the different salts of the reference-acid have the same absorption, the free acid an entirely different one. This behavior is very common, the absorption in the salt solutions is that of the anion, which is the same in all, that of the undissociated acid, being that of an altogether different substance, is different of course. The attention in reading the two papers cited is taxed with much that is due simply to a misunderstanding of the dissociation theory.

Ostwald has recently offered an explanation[4] of the fact that some weak dibasic acids, as succinic acid, may be readily titrated with a colored indicator, whereas certain stronger ones, as phosphorous or sulphurous acids, may not be. He assumes the negative electrical charge of the anion to be localized at that point from which the hydrogen ion has been dissociated, and that the appearance of this charge must hinder the appearance of another negative charge upon the same ion, *i. e.*, the dissociating of the second hydrogen ion of the dibasic acid, and so prevent the complete formation of neutral salt. If the two carboxyls be widely separated, as in succinic acid, this hindering effect is supposed to have so diminished that the neutral salt may be formed, *i. e*, the acid may be successfully titrated. This explanation accords with the facts cited, but hardly with the behavior of the acids of the oxalic acid series, which dissociate their "second hydrogens" ever less with increasing complexity.[5]

[1] Röhmann and Spitzer· Ber. d. chem. Ges. **24**, 3010.
[2] Ann. Chem. (Liebig) **270**, 204; *ibid.* **270**, 208.
[3] Ztschr. phys. Chem. **10**, 671.   [4] *Ibid.* **9**, 553.   [5] Trevor: *Ibid.* **10**, 349.

A simple experiment has shown that the velocity with which methyl acetate is catalyzed by aqueous acids is the same (within 1 per cent.) when the solutions have been made stiff by gelatine (*agar-agar*) as it is in pure water.[1] Also the diffusion-velocities of electrolytes have been found to be in gelatinized water practically the same as in pure water.[2] Both results were to be foreseen, since the partial pressures of the ions are uninfluenced by the addition of the colloid.

The rate of saponification of an ester is proportional to the concentration of the hydroxyl ions of the base used. From the saponification-velocities of inorganic bases with methyl acetate Bugarsky[3] has determined their relative dissociations to be: potash, 1.000; soda, 0.965; lithia, 0.972; baryta, 0.944; strontia, 0.915; lime, 0.911. The agreement with the figures obtained from the conductivities is excellent.

The affinity-constants of thirty organic bases have been determined by Walker[4] from the molecular electrical conductivities of their sulphates and hydrochlorides, as well as from the velocities with which the hydrochlorides catalyze methyl acetate in aqueous solution. This catalysis is effected by the acid set free by hydrolytic action, which decreases in amount on passing from weaker to stronger bases. Bases varying in strength from orthonitroaniline ($= 376$) to quinaldine ($= 89.2$) were investigated.

A discussion between Lothar Meyer and J. H. van't Hoff, upon the theory of solutions, has been brought to an abrupt termination by a most amusing reply of the latter.[5] He shows that all experimental material yet at hand confirms the fundamental law that the osmotic pressure follows the laws of gases. Further, the statement that the theory requires solutions of equal osmotic pressures to have equal freezing-point depressions in different solvents and equal relative decrease of vapor-pressures, is shown to be totally wrong, none of these three sets of solutions being equivalent in fact or in theory.

In a paper by Arrhenius,[6] the law of mass-action has been applied to the study of the equilibria in solutions containing several binary electrolytes (*i. e.*, homogeneous systems), and he has shown that these equilibria are entirely accessible from the dissociation-constants of each possible set of molecules present, since the equilibria depend upon the percentage dissociation of each set as represented by the equation of the dissociation-isotherm

$$Ck = c_1 c_2.$$

Here C, c_1 and c_2 represent the concentrations of the undissociated molecules and of each of the dissociation-products (ions) formed, and k is to be found from conductivity, reaction-velocity, etc. The state of equilibrium between the ions and the undissociated

[1] Reformatsky: Ztschr. phys. Chem. **7**, 34.   [2] Voigtländer· *Ibid.* **3**, 316.
[3] *Ibid.* **8**, 398.   [4] *Ibid.* **4**, 319.   [5] van't Hoff: *Ibid.* **9**, 477.   [6] *Ibid.* **5**, 1 (1890).

molecules, obtaining in a solution of a weak and a strong acid and their sodium salts, is calculated, according to the mass law, from the dissociation-constants of each set of molecules. From the resulting concentration of the dissociated hydrogen is then calculated the thereto proportional inversion-velocity of the action of the solution upon cane sugar, and results agreeing well with direct experiment are obtained. It is further shown, by combining the equations for the dissociation-isotherms of the various dissociation-reactions coming into play, that the so-called "avidity"—the ratio of distribution of two acids with a base—is equal to the ratio of the square roots of the dissociation-constants of the acids, or *approximately* to the ratio of the percentage-dissociations of the acids.

The formulæ are applied further to the phenomena of hydrolysis, *i. e.*, the decomposition of the salts of very weak acids or bases by water, whereby water must be treated as a very slightly dissociated electrolyte. An example of this hydrolytic action, which, be it stated, *demonstrates* the electrolytic partial dissociation of water into hydrogen and hydroxyl ions, is the hydrolysis of the alkali carbonates in the sense of the equation

$$Na_2 \mid CO_3 + 2H : OH \gtrless 2Na \mid OH + H_2 : CO_3;$$
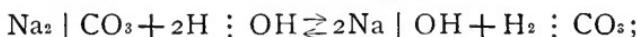
the two weak acids, water and carbonic acid, are so slightly dissociated that only the alkaline reaction of the strongly dissociated sodium hydroxide appears. If we take the salt of a weak base instead of a weak acid, as aniline hydrochloride, for example, the reaction is of the same character,

$$C_6H_5NH_2 \mid Cl + H : OH \gtrless C_6H_5NH_3 : OH + H \mid Cl,$$
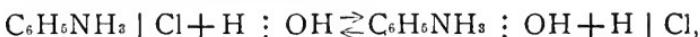
but here the two bases water and aniline hydroxide are so weak that the solution shows only the acid reaction of the strongly dissociated hydrochloric acid.

A third case may be realized if we take the salt of a very weak acid with a weak base, where all products are slightly dissociated, and hence their solution if sufficiently concentrated reacts neutral. Such would be a solution of aniline acetate.

The following theory of the equilibria in saturated salt-solutions —that is to say, of the solubility-equilibria of electrolytes—is a simple application of the principle of mass-action to the conditions of these heterogeneous systems and is due to the brilliant Nernst.[1]

The solubility of a substance depends upon its "solution-pressure."[2] In a saturated salt-solution one equilibrium is maintained between the solid salt and its undissociated, dissolved molecules, proportionality necessarily existing between their concentrations; a second equilibrium existing between these latter and the ions

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[1] Nernst : Ztschr. phys. Chem. **4,** 372. For additional quantitative confirmation see Noyes : *Ibid.* **6,** 241.
[2] See This Journal **15,** 141.

into which they, on the other hand, are transformed, calls for proportionality between the concentrations of undissociated molecules and ions. The concentration of the solid remaining constant, the product of the concentrations of the ions is thus, at constant temperature in saturated solution, also required to be constant. Increasing the partial pressure of one of the ions, by the addition of another electrolyte with a common ion, causes then a partial precipitation of the dissolved salt, *i. e.*, a decrease of its solubility. Thus hydrochloric acid will precipitate chlorides from their saturated solutions, and silver acetate will likewise be precipitated by silver nitrate or a soluble acetate, but not appreciably by acetic acid, since the slightly dissociated acid contains free acet-ions in but minimum amount. This behavior is in every way analogous to the precipitation of ammonium chloride from its vapor by the addition of one of its dissociation-products. In the paper cited this relation is brought into strict mathematical form and is verified quantitatively by suitable experiments.

As a further application of the theory, the influence of eleven different chlorides upon the solubilities of thallous and lead chlorides has been studied[1] for the purpose of determining the degree of electrolytic dissociation of these chlorides. In passing from 0.2- to 0.03-normal solutions, the dissociation was found for hydrochloric acid to increase from 73 to 89 per cent.; for the chlorides of potassium, sodium and ammonium, from 65 to 89; for those of magnesium, calcium, barium, zinc, manganese and copper, from 62 to 82; for cadmium chloride, 32 to 60. From these figures far more satisfactory dissociation-constants were obtained for the chlorides of the univalent metals than from the electrical conductivities of their solutions. For the chlorides of the bivalent metals a constant was not obtainable.

Nernst's theory of the solubility of a compound in the presence of one of its dissociation-products has been successfully applied by Behrend[2] to alcoholic solutions of phenanthrene picrate, containing an excess of phenanthrene or picric acid. In his first paper it is further shown that, in saturated alcoholic solutions, the products of the concentrations of benzyl isoparanitrobenzaldoxime and paranitrobenzyl isobenzaldoxime, which are the dissociated components of a double compound, remain constant no matter what excess of one or the other component be present. This follows from the proportionality of the concentration of the undissociated double compound, to that of the undissolved solid with which it is in equilibrium (mass law), the concentration of the solid being of course constant; and the proportionality of the former concentration to that of the dissociation-products, with which it in turn is in equilibrium. The dissociation of the compound is very complete—about 90 per cent.—as was shown by special experiments. The solubilities were determined by a suitable analytical

[1] Noyes: This Journal **9**, 603.   [2] *Ibid.* **9**, 405; **10**, 265.

method. Deducting the amount of undissociated compound present, a most satisfactory constant was obtained. The paper is a very neat contribution to the study of the equilibria in solutions of organic compounds.

An electrolytic synthesis of dibasic acids has been developed by Crum Brown,[1] the method consisting in the electrolysis of the ester salt of a dibasic acid, whereby CO_2 splits off from the anion, which then unites with itself to form the di-ester of a more complex acid. Thus, from malonic acid was prepared succinic acid :

$$COOC_2H_5.CH_2.\overline{COO + COO.CH_2}.COOC_2H_5 =$$
$$COOC_2H_5.CH_2.CH_2.COOC_2H_5 + 2CO_2.$$

In a paper on the aqueous solutions of double salts,[2] convincing evidence has been adduced for the distinction between true double salts, as the alums, which, not existing independently in solution, give the reactions of their components, and the salts of complex acids, as Na_2PtCl_6, which do not do so. This distinction has been clearly understood ever since the classical investigations of Hittorf, in 1859, on the phenomena of electrolysis, and in this paper the conductivities of these salt solutions have been shown to require the simple distinction indicated. It will be remembered that the same conclusion must be drawn from the diffusion experiments of Graham and Rüdorff, who found the components of the true double salts to diffuse independently, while those of the salts of the complex acids do not; and from the evolution of heat in the formation of the latter, while no thermal evidence for the formation of the former in solution is obtainable.

Other interesting work upon dissociation-phenomena has recently appeared, which, although by no means electrolytic, may be profitably considered in this connection. The vapor-densities of sulphur vapor between 467.9° and 606.0° C. have been determined, with the aid of the Dumas method, by Biltz.[3] His observations have been calculated by Riecke,[4] from the potential theory of Willard Gibbs; the result indicating that normal molecules, S_8 first appearing, break up into $S_6 + S_2$, the S_6 molecules dissociating in turn into $3S_2$ as the temperature rises. It will be remembered that above 800° the molecular formula of sulphur remains constant as S_2. It appears, then, that the normal molecule is S_8, but that the boiling-point of sulphur lies above the temperature at which dissociation begins. This view is beautifully confirmed by molecular-weight determinations at a still lower temperature, the boiling-point of carbon bisulphide, made by Beckmann with the aid of the boiling-point method.[5] A mean value of 261 was obtained; S_8 requires 256. One experiment gave 255.

The molecular weight of iodine dissolved in ethyl ether and in

[1] Crum Brown and Walker: Ann. Chem. (Liebig) **261,** 107.
[2] Kistiakowsky: Ztschr. phys. Chem. **6,** 97.   [3] *Ibid.* **2,** 920.   [4] *Ibid.* **6,** 430.
[5] Beckmann: *Ibid.* **5,** 76 (1890).

carbon bisulphide, and that of phosphorus dissolved in carbon bisulphide, were likewise determined; the molecular formulæ found were I_2 and P_4, respectively.

The dissociation of nitrogen peroxide in solution in chloroform has been studied by Cundall,[1] the amount of dissociation being determined by a colorimetric method. The percentage dissociation increased with diminishing concentration and with rising temperature. Ostwald[2] has calculated the results according to the formula for binary dissociation, $a^2/(1-a)v = k$, and obtained a satisfactory constant, thus showing the dissociation in this solution to follow the same law as in the gas. The dissociation is here, however, far less in degree.

By application of the second law of thermodynamics, the effect of temperature change upon chemical equilibrium has been expressed in very simple form by van't Hoff.[3] In the familiar thermodynamical equation connecting pressure and temperature changes,

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{1}{T} \left(\frac{\partial Q}{\partial v} \right)_T ,$$

the heat $\partial Q/\partial v$ added in unit increase of volume at constant temperature, decreased by the work $p.\varDelta v = p$ done in the expansion, whereby x per cent. of substance is transformed, is the *heat of reaction* involved $\left(\frac{\partial x}{\partial v} \right)_T q$, q representing the molecular heat of reaction. Eliminating Q above, and substituting for $\left(\frac{\partial \frac{p}{T}}{\partial T} \right)_v$ its value obtained from the gas equation $pv = [n(x-1) + n'x]$, n initial and n' transformed molecules being involved in the reaction, there results

$$\left(\frac{\partial x}{\partial v} \right)_T q = \frac{RT^2}{v} (n' - n) \left(\frac{\partial x}{\partial T} \right)_v .$$

By expanding and differentiating the Mass-Law equation

$$\frac{\left(\frac{x}{v} \right)^{n'}}{\left(\frac{1-x}{v} \right)^n} = K ,$$

these differential coefficients of x are eliminated, yielding as final result,

$$\frac{\partial \log K}{\partial T} = \frac{q}{RT^2} ,$$

[1] J. Chem. Soc. 1891, 1076.   [2] J. Chem. Soc. 1892, 242.
[3] Van't Hoff: Kongl. Sv. Vet.-Akad. Handlingar, **21**, No. 17; also Arch. neerl. **20**, 239.

the change with temperature (at constant volume) of the equilibrium-constant K, as function of the molecular heat of reaction q. Depending upon the character of the reaction, q may be the so-called heat of vaporization, of sublimation, solution, dissociation, or of any reaction more strictly chemical. The integral of this equation

$$\log_e K_2 - \log_e K_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

has been used for calculating many various heats of reactions,[1] of which the following are examples:

Reaction.	$\delta p =$ change of	q calc.	q obs'd.
Vaporization of water.	vapor-pressure.	10100 cal.	10296 cal.
Dissolving succinic acid in water.	solubility.	6900 "	6700 "
Sublimation of ammonium hydrosulphide.	dissociation-pressure.	21550 "	21640 "
$BaCl_2 + 2H_2O =$ $BaCl_2\,2H_2O$.	tension of water vapor.	3815 "	3830 "
$N_2O_4 = 2NO_2$.	(found from densities).	12900 "	12500 "

Le Chatelier[2] has reversed this procedure, by calculating the percentage dissociation of carbon dioxide (reaction $2CO_2 = 2CO + O_2$), at different temperatures and pressures, from the heat of combustion of carbon monoxide. The agreement with such values as are known is excellent, other values are

at 1000° and 1.000 atm.	0.06 per cent.
3000° " 1.000 "	40.
3000° " 0.001 "	94.

An attempt has been made by Arrhenius[3] to calculate the heats q of electrolytic dissociation of certain acids and salts in aqueous solution, by a direct use of the differential equation $\dfrac{\delta \log K}{\delta T} = \dfrac{q}{RT^2}$, setting for $\delta \log K$ the change of K between 18° and 52°, as determined from measurements of electrical conductivity. The heats of dissociation found in this way are in all cases strikingly small, rarely exceeding 1000 gram-calories, and are mostly negative. It may here be remarked that if q in such cases be zero, or nearly so, the electrolytic dissociation is entirely, or practically, independent of the temperature. Recent experimental results of the writer[4] have in fact shown this dissociation for all classes of organic acids to remain practically unchanged through a temperature range of 25° to 100° C.

According to the theory of electrolytic dissociation, the heat of neutralization of an alkali with an acid is a summation of the heats

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[1] A critical collection of this material is given in Nernst (Dammer's Handbuch der anorg. Chemie, Allg. Teil), 311-318 (1892).
[2] *Ztschr. phys. Chem.* **2**, 782. [3] *Ibid.* **4**, 96; corrected results given *ibid.* **9**, 339.
[4] Trevor: *Ibid.* **10**, 338.

of dissociation of their undissociated portions and of that of the salt formed, *plus* the heat of formation of water from hydrogen and hydroxyl ions (the heat of electrolytic dissociation of water). From the above results, and the observed heats of neutralization, Arrhenius calculated this heat of dissociation of water to be 13520 gram-calories at 21.5°.

Still another important result has been yielded by the equation $\frac{\delta \log K}{\delta T} = \frac{q}{R T^2}$. It is evident that, since R and T are essentially positive quantities, $\delta \log K$ and q must have the same sign; *i. e.*, *if a reaction* $\begin{cases} absorb \\ evolve \end{cases}$ *heat it* $\begin{cases} advances \\ retrogrades \end{cases}$ *as the temperature rises.* This extremely important principle has been termed by van't Hoff "Principe de l'équilibre mobile."

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NOTES.

On the Spreading of Solutions in Filter Paper.

From the work of Schönbein, Bayley, Goppelsröder and others, it is known that when dilute solutions of salts are absorbed by porous paper, the water spreads beyond the dissolved substance : thus, when a drop of a dilute solution of potassium hydroxide falls on filter paper, it is found that the outer rim of the wet area responds to no test for the alkali, but contains water only. Furthermore, when several substances are present in the solution, some of them will spread over wider limits than the others. It appears from the present investigation that of two salts, the one which has the greater velocity of diffusion spreads more rapidly in the paper.

Emil Fischer and Edward Schmidmer make use of these facts in the study of certain double salts and other complex compounds.[1] Their apparatus consists of a glass tube 70 cm. long and 2 cm. inner diameter, in which are placed, end to end, six cylinders of porous paper, each 10 cm. in length. This tube is allowed to dip into the solution, so that the bottom of the lowest cylinder is wetted by it, and is left there until the liquid has risen so that the fifth cylinder is completely wetted; this usually requires from three to four days. The determination is then made by washing out the salts contained in one of the cylinders, generally the third, fourth or fifth, and analyzing the solution thus obtained, in the usual way.

[1] Ann. Chem. (Liebig) **272**, 156.

The following are the main results of the investigation:

A 10 per cent. aqueous solution of ferrous ammonium sulphate, $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$, gave in the fourth roll:

$$0.0242 \text{ gram } Fe_2O_3,$$

corresponding to 0.0169 gram Fe

and $\qquad$ 0.0173 gram NH_3

If the proportion of iron to ammonia in the compound be taken as 1 : 1, then that found in the cylinder is as 1 : 1.686, proving that the ammonium sulphate had travelled farther than the ferrous sulphate, and, hence, that the double molecule was dissociated into ammonium sulphate and ferrous sulphate.

With a cold saturated solution of the same salt the proportion was

(1) as 1 : 1.004
(2) as 1 : 0.993

in two experiments.

Ferrous potassium sulphate and nickel sodium sulphate were investigated in the same way, the results being, in general, in accordance with the above, and showing that in dilute solution these salts suffer dissociation in a high degree; in concentrated solution, on the contrary, no evidence of dissociation can be observed.

A study of the double chlorides of mercury with sodium, lithium and ammonium shows that the first two are dissociated in a 20-per cent. aqueous solution, but not in an alcoholic solution of the same concentration, whereas the chloride of mercury and ammonium is not dissociated in either solvent.

Other investigators (van Bemmelen, Rüdorff and others) had already shown that the double salts of phosphoric and hydrocyanic acids, and of the polybasic organic acids, are for the most part not dissociated. An investigation by the present method leads to the same conclusion, the following salts being the ones used:

Sodium ammonium phosphate $HNa(NH_4)PO_4 + 4H_2O$, potassium silver cyanide $KCN.AgCN$, and potassium sodium tartrate $KNaC_4H_4O_6 + 4H_2O$. The compound of grape sugar with sodium chloride, $2C_6H_{12}O_6 + NaCl$, is found to undergo dissociation in a 10-per cent. solution in water.

The authors have also studied solutions in alcohol and acetone of naphthalene picrate $C_{10}H_8.C_6H_2(NO_2)_3.OH$, and methylketol picrate $C_9H_9N.C_6H_2(NO_2)_3OH$, but find no evidence of dissociation in either case.

Finally, some experiments were performed for the purpose of comparing the present method with the older one used by Graham and Rüdorff, in which diffusion was allowed to take place through a membrane: the result goes to show that the older method is more rapid for aqueous solutions, but for solutions in alcohol the newer method is to be preferred, since in such cases diffusion goes on very slowly through a membrane. A. P. SAUNDERS.

AMERICAN

CHEMICAL JOURNAL.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

V.—ON THE REACTION OF CERTAIN ALCOHOLS WITH PARA-DIAZOMETATOLUENESULPHONIC ACID.[1]

By W. V. METCALF.

Introduction.

Some time since it was desired to obtain a considerable quantity of metatoluenesulphonamide. Several methods of making the compound were on record, two of which were adapted to preparing it in quantity. In 1873 F. C. G. Müller[2] obtained it by reducing the barium salt of orthobrommetatoluenesulphonic acid by sodium amalgam and treating the product with phosphorus pentachloride and ammonia.

$$C_6H_3 {<}^{CH_3}_{\diagdown SO_3H(m)} \text{—Br}(o) + H_2 = C_6H_3{<}^{CH_3}_{SO_3H} + HBr.$$
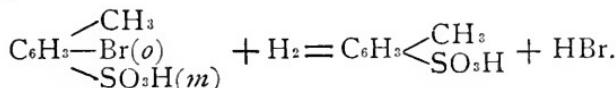
The following year v. Pechmann[3] obtained it by boiling paradiazo-metatoluenesulphonic acid with alcohol under a pressure of 200 mm. of mercury and treating the product with phosphorus pentachloride and ammonium hydrate.

$$C_6H_3 {<}^{CH_3}_{\diagdown N_2(p)} \text{—}SO_3(m) + C_2H_5OH = C_6H_3{<}^{CH_3}_{SO_2H} + C_2H_4O + N_2.$$

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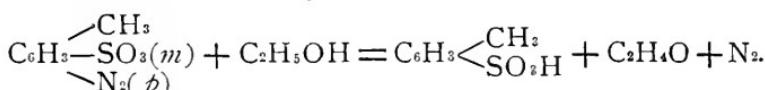
[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1890.

[2] Ann. Chem. (Liebig , **173**, 195.   [3] *Ibid.* **169**, 47.

It was observed, however, that the products obtained by the different processes were not identical. The difference lay principally in the melting-points of the amides, and in the solubility and water of crystallization of the salts of the corresponding sulphonic acids. Professor Remsen suggested to me that probably the discrepancies were due, in part at least, to the fact that the reaction did not take place wholly as v. Pechmann supposed, that there was formed also a certain amount of the ethoxy amide, which remained mixed with the metatoluenesulphonamide as an impurity. The reaction in this case would be

$$C_6H_3\overset{\diagup CH_3}{\underset{\diagdown N_2}{-}}SO_2 + C_2H_5OH = C_6H_3\overset{\diagup CH_3}{\underset{\diagdown O.C_2H_5}{-}}SO_3H + N_2.$$
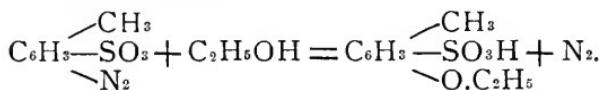
It was determined to test this hypothesis by a careful study of the action of alcohol on the diazo compound in question.

Preparation of Paratoluidinemetasulphonic Acid.

The paratoluidinemetasulphonic acid was made from paratoluidine according to the method of v. Pechmann.[1] To 100 grams of paratoluidine were added 200 grams of fuming sulphuric acid. Thereupon the mass heated, turned dark, and gave off fumes of sulphur dioxide. (It was found afterward that the yield was somewhat better if the paratoluidine was added gradually to the fuming sulphuric acid, with frequent stirring, thus preventing the temperature from rising too high.) The mixture was then kept at a temperature of 180° for about an hour. The heating should be stopped and the mass allowed to cool as soon as the odor of the sulphur dioxide fumes given off becomes marked. v. Pechmann's work has shown that if the heating is continued beyond this point, the comparative yield of paratoluidineorthosulphonic acid and of the disulphonic acid is much increased. After cooling, the material was poured into twice its volume of water; the mixed sulphonic acids crystallized on standing, giving a dark gray, semi-liquid, pasty mass; the liquid was drained off from this mass, as completely as possible, with a filter-pump and afterward by heavy pressure between the plates of a screw-press. The liquid thus obtained was very dark, almost black. On standing for two or three weeks there crystallized out from it a considerable quantity

[1] Ann. Chem. (Liebig) **173**, 195.

of long, thin plates apparently belonging to the triclinic system. These were purified by boiling with animal charcoal and by recrystallization. By this treatment they were obtained in a pure white condition, but were not examined further. In all probability they were crystals of the paratoluidinedisulphonic acid mentioned by v. Pechmann. The dark mass that remained after pressing the liquid out consisted principally of the meta- and orthosulphonic acids of toluidine. The remaining sulphuric acid was precipitated by an excess of barium hydroxide solution. The solution was then boiled briskly for some time to drive off any toluidine that might have remained unacted upon by the sulphuric acid. (As a rule, this was found unnecessary, but occasionally there remained quite an excess of unchanged toluidine.) The excess of barium was then precipitated as accurately as possible with sulphuric acid, the barium sulphate filtered off and the filtrate evaporated to crystallization. It was found that considerable quantities of the sulphonic acids were precipitated with the barium sulphate. It was therefore necessary to boil the precipitate several times with water, filter, and add this wash-water to the original filtrate in order to avoid serious loss of material. This is especially true when the solution is too concentrated. It is best to work with a large amount of water—say 8 to 10 liters for every 100 grams of the original toluidine. The solution, freed from barium and sulphuric acid—(a slight excess of sulphuric acid does no harm)—was evaporated until it began to crystallize, and then allowed to cool. On cooling, long, beautiful, sulphur-yellow needles of the meta acid crystallized out, seeming to fill the whole dish. The appearance is very deceptive, as the crystals shrink to a small bulk when filtered. They were filtered off and the mother-liquor evaporated nearly to dryness, and allowed to crystallize. A considerable quantity of the rhombohedral crystals of the ortho acid were obtained from the mother-liquor, some also from the first crystallization of the meta acid. The two acids may be separated either by the difference in the solubility of the lead salts or of the potassium salts, or by crystallizing the acids themselves from dilute alcohol.[1] The latter method was found more convenient and satisfactory, involving less loss of material.

If the needles of the meta acid are small (which result may be obtained by crystallizing rapidly with stirring), an almost com-

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[1] Ann. Chem. (Liebig) **173**, 197; This Journal **8**, 274.

plete separation may be secured through the difference in the specific gravity of the two acids. The mixed acids were shaken up with a considerable quantity of dilute alcohol (say fifty-per cent.), and, after partial settling, the light needles of the meta acid were poured off. By repeated shaking and settling and pouring back and forth (*i. e.*, by a sort of fractional decantation), the two acids may be obtained in a nearly pure condition. The separation is completed by a single crystallization from dilute alcohol in which the ortho acid is but very slightly soluble. The meta acid still retains a yellow color which it is difficult to remove. It may be obtained, however, in a pure white condition by repeated boiling with animal charcoal and by recrystallization.

Preparation of Paradiazometatoluenesulphonic Acid.

v. Pechmann [1] recommends diazotizing the meta acid by suspending either in alcohol or water and treating with nitrous acid. Later it was shown, however, that on account of the solubility of the diazo compound in water it is preferable to use alcohol.

Notwithstanding this, water was used as the medium in the first experiments tried. It was kept cool and a rapid stream of nitrous fumes passed through it. The reaction took place very rapidly. Some twenty grams of the acid were diazotized in less than ten minutes, the product being of a very faint pink tinge, nearly white. The yield, however, was very poor—less than fifty per cent. of the theoretical. A large proportion of the diazo compound remained in solution in the water, from which it could not easily be separated.

In all subsequent experiments ninety-two per cent. of alcohol was used (say 250 cc. to 25 grams of the acid), and was found to work very satisfactorily. The alcohol in which the finely pulverized acid was suspended was placed in an Erlenmeyer flask. On passing the nitrous fumes through it it gradually becomes hot, turning yellow, and finally a bright yellowish red   The yellow acid then changes rapidly over to the pink or pinkish white grains of the diazo compound. The whole process requires about thirty minutes. While the alcohol remains cold, little or no action takes place. By the action of the nitrous fumes the material is heated in ten or fifteen minutes, but time is saved by heating the alcohol to 26°–30° before beginning the operation. The temperature

[1] Ann. Chem. (Liebig) **173**, 201.

should not be allowed to rise above 40°, otherwise there is danger of considerable decomposition. The temperature may easily be regulated when there is danger of too great heat, by placing the flask in a dish of cold water. The higher the temperature at which the action takes place the darker is the pink color of the resulting diazo compound. By careful treatment, especially if absolute alcohol be used, the product may be obtained in a very nearly pure white condition. The action is hastened by continual shaking. When the action is complete the diazo compound is filtered by means of a filter-pump, washed with alcohol and then with a little ether. The yield is very good—eighty-five to ninety-five per cent. of the theoretical. 50–100 grams of the acid may conveniently be diazotized at one time. The diazo compound, if perfectly dry and kept in the dark, remains unchanged for a long time; if left in a moist condition it rapidly turns yellow. Even the dry compound gradually decomposes when exposed to the light, though it may be kept for several days without undergoing any change.

It is interesting to note in passing that the metasulphonic acid of paratoluidine is more easily diazotized than the corresponding ortho acid, both in water and in alcohol. In several of the diazotizing experiments that were tried, the meta acid used contained a small amount of ortho acid as an impurity. In these cases there remained invariably a residue of the ortho acid after all the meta acid had passed over into the diazo compound. The same fact was observed when water was used as the medium in which the acid was suspended. To test the point more carefully two grams of the acid were ground up together, and ninety-two per cent. of alcohol added to the mixture; nitrous fumes were passed through it for about thirty minutes; there then remained a considerable residue of the unchanged ortho acid, while all of the meta acid had been converted into the diazo compound. The mixture was shaken rapidly during the whole of the diazotizing process, to prevent any separation of the two acids by the difference in their specific gravity. The experiments show that the meta acid is more easily diazotized than the ortho acid.

Action of Ethyl Alcohol on Paradiazometatoluenesulphonic Acid.

Twenty-five grams of the diazo compound were boiled with 400 cc. of alcohol (98-per cent.) under a pressure of 195–210 mm.

of mercury in the apparatus used by Remsen and Palmer,[1] and by Remsen and Dashiell.[2] At first there appeared to be no change, but soon the alcohol began to turn yellow, then gradually changed through orange color to a dark red. The suspended diazo compound meanwhile had been dissolved, leaving a clear red solution. During the boiling there was a slight odor of aldehyde. The reaction is completed when the diazo compound is entirely dissolved. This took place in about twenty-five minutes, but the boiling was continued for some time.

In a subsequent experiment 20 grams of the diazo compound were boiled with 300 cc. of alcohol (98-per cent.) under 400 mm. pressure. The solution seemed to be complete in ten minutes, but the boiling was continued for half an hour. In this experiment also there was only a slight odor of aldehyde.

The dark red liquid obtained in this way was strongly acid in its reaction. It was heated to boiling on a water-bath, and neutralized, as nearly as possible, with dry sodium carbonate. The neutral or slightly alkaline solution was then evaporated to dryness on a water-bath, and finally powdered and dried in an air-bath. It was found in the experiments that if any water was mixed with the solution, the process of drying was an exceedingly tedious one. On evaporating it formed a dark brown, gummy mass from which it was very difficult to drive off all the water. If, however, all the water was carefully excluded, the strong alcoholic solution evaporated and dried rapidly. The dried sodium salt was finely pulverized and treated with somewhat more than an equal weight of phosphorus pentachloride. After the reaction there remained a red oil. This was washed in a large amount of cold water and treated with concentrated ammonia solution, in the usual way, to form the amide. On adding ammonia the substance became hot, assumed a bright yellow color, and gradually became solid. After the completion of the reaction the ammonia was evaporated on a water-bath, and there remained a dark red, gummy, semi-crystallized mass. This was boiled repeatedly with a large amount of water until nearly all was dissolved. There remained undissolved a small amount of a dark brown, tarry substance. The water, with the substance in solution, was filtered and allowed to cool, when there crystallized out a considerable quantity of yellowish needles, mixed with more or less gummy

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[1] This Journal **8**, 243. [2] *Ibid.* **15**, 105.

material. This was boiled with animal charcoal and recrystal-
lized five times, and thus the substance was obtained in the form
of pure white needles with a constant melting-point 138°–139°.
(The metatoluenesulphonamide, obtained by v. Pechmann, crystal-
lized in rhombohedral scales and melted "somewhat below 100°.")
The compound is moderately soluble in boiling water, but very
slightly so in cold water. It dissolves easily in cold alcohol, ether,
and acetone. Hot benzene dissolves it readily. Analysis showed
its composition to be $C_9H_{13}O_3NS$. The results obtained were as
follows:

.20251 gram of the substance gave .2205 gram barium sulphate
$= 14.97$ per cent. S. The determination was made by Liebig's
method. (Two determinations were made by Pearson's method
which gave an average 0.51 per cent. too low. Other determina-
tions, in this laboratory, by Pearson's method, of certain diffi-
cultly decomposable sulphonamides have given similar results.)

.25100 gram of the substance gave ammonia equivalent to
10.86 cc. of a standard ammonia solution containing 1.4672 grams
of nitrogen to the liter.

.24822 gram of the substance gave .45478 gram of carbon
dioxide and .1341 gram of water.

For $C_9H_{13}O_3NS$:

		Theory.	Found.
C_9	108	50.23	49.96
H_{13}	13	6.05	6.00
O_3	48	22.33	…
N	14	6.51	6.35
S	32	14.88	14.97
	215	100.00	

The compound formed was undoubtedly paraethoxymeta-
toluenesulphonamide, $C_6H_3\underset{\diagdown O.C_2H_5(p)}{\overset{\diagup CH_3}{-}SO_2NH_2(m)}$.

This is one of some thirty known cases in which a diazo com-
pound boiled with alcohol gives a substance·in which the diazo
group is replaced by the ethoxy group instead of by hydrogen.
The yield of the ethoxy compound was poor; of the purified
substance there was obtained only a little over nine per cent. of
the theoretical. The actual yield was of course considerably larger,

there being more or less loss of material in the repeated crystallizations necessary for purification. The small yield of the ethoxy compound suggests, of course, that most of the diazo compound was acted upon in the regular way, giving the reaction

$$C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown N_2(p)}{-}}SO_3(m) + C_2H_5OH = C_6H_4{<}{\overset{CH_3}{SO_3H(m)}} + C_2H_4O + N_2.}$$
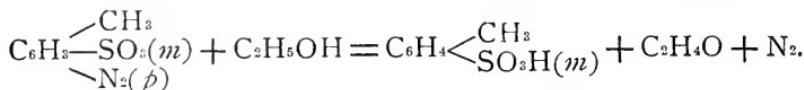
But the absence of any strong odor of aldehyde during the reaction renders it improbable that the metatoluenesulphonic acid was produced to any considerable extent. To determine this point accurately, all the mother-liquors of the different crystallizations of the ethoxy compound were worked over with great care. There was obtained, in this way, a small quantity of a mixture made up evidently of the small rhombic scales of metatoluenesulphonamide, together with more or less of the paraethoxy derivative of the same. With the small quantity at hand it was found impossible, by repeated crystallizations, to separate the two compounds completely. Possibly with larger quantities this might be effected more easily. The different crystallizations made in the effort to purify the metasulphonamide gave various mixtures melting between the points 98° and 108°. Usually the mixtures had no sharp melting-point, but melted through several degrees. A few mixtures were obtained, however, that seemed to have a fairly definite melting-point. One, for example, melted quite sharply at 105°, and recrystallization in a small amount of water in a test-tube produced little change. By recrystallizing in a large amount of water, however, and filtering off the first of the material that crystallized out, a small quantity of the ethoxy derivative was obtained in a nearly pure condition.[1]

The experiments prove beyond question that the two amides crystallize together in mixtures that are exceedingly difficult to separate and which might easily be mistaken for approximately pure substances. It is highly probable that this fact furnishes an explanation of the hitherto unexplained discrepancies between the metatoluenesulphonic acid made from the diazo compound and that made according to Müller. The sulphonamide which v. Pechmann obtained from the diazo compound had no definite melting-

[1] Nevile and Winther (Ber. d. chem. Ges. **13**, 1947, and Journ. Chem. Soc. **37**, 625) give 106.5°–107.5° as the melting-point of the amide obtained by them in small quantity.

point. He speaks of it as melting "somewhat below 100°." It was probably a mixture of the two amides.

Preparation of Paraethoxymetasulphaminebenzoic Acid.

Five grams of the ethoxy amide were placed in a flask, together with 190 cc. of water and 1.8 grams of caustic potash, and heated in a water-bath until the amide was entirely dissolved. There was then added a hot solution of 8 grams of potassium permanganate in 190 cc. of water. The whole was heated in a water-bath until the color disappeared, leaving a yellow liquid above the dark brown deposit of manganese hydroxide. This, on cooling, deposited a considerable quantity of the unchanged amide. More potassium permanganate was therefore added, and the heating was continued until decolorization took place. The manganese hydroxide was then filtered off and the liquid allowed to cool. After filtering to remove the small amount of unchanged amide which crystallized out, the solution was acidified with hydrochloric acid. This gave a copious precipitate of fine white needles. In order to remove the small amount of the original amide which was contained in the precipitate, it was first dissolved in hot dilute sodium carbonate, and the solution evaporated to dryness. The dried mass was treated with a small amount of cold water, the solution filtered, and the filtrate acidified. The pure white needles obtained in this way were recrystallized from water. They were almost insoluble in cold and difficultly soluble in boiling water. The solution gave a strongly acid reaction. Two and a half grams of the substance were obtained in long, beautiful needles which seemed to be perfectly pure. It melted at 220°–230°, with gradual decomposition, as shown by the brown color which deepened as the temperature rose. For fear that this indicated impurity, the whole was converted into the barium salt by neutralizing the boiling solution with pure barium carbonate. The filtrate was evaporated to dryness, and thus the barium salt was obtained in the form of fine, pure white needles, only moderately soluble in cold water, but very slightly soluble in hot absolute alcohol. The salt was boiled in absolute alcohol to remove the last traces of the original amide, and then recrystallized once from water. After determining the water and barium in this salt, it was dissolved and the acid again precipitated with hydrochloric

acid. It was then washed thoroughly and recrystallized once from water. A determination was made of the nitrogen in the acid so obtained. The analyses gave for the barium salt the formula $C_{18}H_{20}O_{10}N_2S_2Ba.2H_2O$, and for the acid the formula $C_9H_{11}O_5NS$.

.1661 gram of the barium salt gave .00899 gram of water (at 210°) and .0588 gram of barium sulphate. This gives for water 5.41 per cent.—theory 5.45 per cent.—and for barium 20.80 per cent.—theory 20.70 per cent.

	For $C_{18}H_{20}O_{10}N_2S_2Ba.2H_2O$.	
	Theory.	Found.
H_2O	5.45	5.41
Ba	20.70	20.80

.2099 gram of the acid gave NH_3, equivalent to 8.047 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter. This gives for nitrogen 5.63 per cent.; theory, 5.71. The acid contained no water of crystallization.

These analyses prove the essential purity of the acid, but the melting-point was still by no means sharp. The material melted mostly at 230°–231°. It showed signs of melting, however, at 225°. The molten substance had a brown color, indicating partial decomposition.

By fusion with potassium hydroxide this acid passes over easily into protocatechuic acid, as was to be expected.

Action of Methyl Alcohol on Paradiazometatoluenesulphonic Acid.

The study of the action of ethyl alcohol on paradiazometatoluenesulphonic acid naturally suggested the question whether methyl alcohol would act in the same way. The question was tested, and the results obtained were, in general, analogous to those obtained in the case of ethyl alcohol. The reaction was found to work more perfectly, however, with the methyl alcohol.

18.5 grams of the diazo compound were boiled with methyl alcohol for fifty minutes, under a pressure of 450 mm. The temperature of the alcohol boiling at this pressure was 78°. Under ordinary pressure it distilled over between the limits 65°–66°. As the diazo compound dissolved, the color turned clear dark red, resembling in appearance the corresponding liquid obtained with ethyl alcohol. The solution was heated nearly to boiling in an

evaporating-dish, and then neutralized with dry sodium carbonate. The sodium salt so formed was difficultly soluble in methyl alcohol. It was precipitated so copiously that the whole became semi-solid, even before neutralization was complete. The salt was then partially dried on the water-bath, and finally pulverized, and the drying completed in an air-bath at 110°. If all water be carefully excluded, the whole process of drying requires less than an hour. The salt so obtained was a light brown, nearly white powder.

Preparation of Paramethoxymetatoluenesulphonic Chloride.

Treated with an equal weight of phosphorus pentachloride and washed with cold water, the sodium salt gave a dark brown oil, much lighter colored, however, than the corresponding ethyl compound. This oil solidified, on cooling, to a semi-crystalline mass. By several recrystallizations from commercial benzene it yields a pure crystalline substance of a faint yellow, or cream, color. Long boiling with animal charcoal and repeated crystallizations failed to remove this color. It melted sharply at 84°. It is easily soluble in cold ether and acetone. In boiling benzene it dissolves readily, and is deposited again, almost completely, as the solution cools. Benzene, therefore, forms the best solvent from which to recrystallize it. In boiling water it dissolves slowly, with decomposition. When crystallized rapidly from a concentrated solution it comes down in the form of fine needles; by spontaneous evaporation from benzene, in beautiful aggregates of large orthorhombic plates. By spontaneous evaporation of a long, narrow column of the ether solution, thicker crystals were obtained, showing a greater variety of faces. The following planes were observed: basal plane, prism, macropinacoid, brachypinacoid, macrodome, brachydome, and perhaps the pyramid. The crystals were shown to belong to the orthorhombic system by the interference figures and the parallel extinction.

A chlorine determination indicated the following formula: $C_8H_9O_3SCl$.

.12349 gram of the chloride gave .0799 gram of silver chloride. This gives chlorine 16.01 per cent.—theory, 16.06 per cent. This analysis was confirmed, as will be described later, by analysis of the corresponding amide and of various salts of the corresponding acid.

The best yield that was obtained was a little less than fifty per cent. of theoretical.

On working over the benzene mother-liquors a small amount of a red oil was obtained, insoluble in cold water, soluble with decomposition in boiling water, forming a solution with which silver nitrate gives a copious precipitate of silver chloride. This oil was not examined with care, but was, in all probability, the meta-sulphon chloride of toluene. The corresponding amide was formed by treating the oil with concentrated ammonia, but the quantity was so small that it was impossible to identify it clearly. It is certain that this action takes place, to some extent, in connection with the methoxy reaction, as will be shown later in connection with the amide.

Preparation of Paramethoxymetatoluenesulphonic Acid.

In order to obtain the acid corresponding to the methoxysulphonic chloride, ten grams of the purified chloride were boiled with about one liter of distilled water for an hour and a half (a balloon flask with an inverted condenser being used to prevent loss). At the end of this time the solution was nearly complete. There remained only a slight impurity suspended in the fluid. The solution, when filtered, was colorless. On evaporating it turned somewhat brown and yielded long, yellowish needles, quite easily soluble in water. These were dissolved, boiled with animal charcoal and filtered. In this way a perfectly colorless solution was obtained, but on evaporation it again turned brown, yielding a crystalline substance which still had a yellowish color. The melting-point also indicated that the substance was impure. Its solution contained a small amount of sulphuric acid, which must have come from the decomposition of the acid. It was found, however, that this acid, when dissolved in water and purified with animal charcoal, yielded pure salts with the carbonates of barium and lead.

In order to obtain a pure specimen of the acid, two or three grams of the pure lead salt were made (see below). This was dissolved in water and the lead precipitated from the solution by hydrogen sulphide. The perfectly colorless solution left after filtering off the lead sulphide, was evaporated over a water-bath. This also turned dark as it approached concentration and gave a brown product. Another portion of the lead salt was then prepared and precipitated by hydrogen sulphide, and the colorless

solution thus obtained was evaporated on a water-bath until it began to have a faint yellowish tinge. It was then allowed to evaporate spontaneously in a vacuum. After four or five days the evaporation was complete and the acid was obtained in a nearly pure condition. It still had a yellowish brown color, however. Undoubtedly, the perfectly pure acid is white. The acid melted at 92°-95°. It evidently decomposes somewhat on evaporation over a water-bath. It was not analyzed, as its composition was sufficiently plain from the mode of formation and the analysis of its salts.

Barium Salt.—The barium salt which crystallizes in needles is exceedingly soluble in water ; slightly, if at all, soluble in cold alcohol or ether. It is moderately soluble in boiling alcohol. Barium determinations gave the following result :

I. .27888 gram of the salt gave .12070 gram of barium sulphate.
II. .29986 gram of the salt gave .12947 gram of barium sulphate.

$$\text{For } Ba\left(C_6H_3{-}SO_3^{\diagup CH_3}_{\diagdown O.CH_3} \right)_2.$$

	Theory.	Found.
Ba	25.39	25.43–25.37

The specimen analyzed was obtained by evaporating the solution to dryness on a water-bath. So prepared, it contained no water of crystallization.

Calcium Salt.—This salt crystallizes in white or slightly yellowish needles. It is exceedingly soluble in water, difficultly soluble in cold alcohol. It dissolves much more easily in boiling alcohol, but, like the barium salt, it does not crystallize easily from this medium except by spontaneous evaporation. There seemed to be a strong tendency to form a supersaturated solution from which the salt would not separate except by evaporation. It is strongly hygroscopic. After drying on a water-bath it absorbs water rapidly, but takes up no definite amount, as was shown by several determinations. It cannot be dried in a desiccator. The salt was dried at 170°, and then three determinations of the calcium were made, which gave the following results :

.21276 gram of the salt gave .06763 gram calcium sulphate.
.17400 gram of the salt gave .05562 gram of calcium sulphate.
.01481 gram of the salt gave .0371 gram of calcium sulphate.

$$\text{For Ca}\left(C_6H_3 \overset{\diagup CH_3}{\underset{\diagdown O.CH_3}{-SO_3}} \right)_2.$$

	Theory.	Found.
Ca	9.03	9.33–9.38–9.38

Lead Salt.—From a concentrated solution the salt crystallizes in white needles. The salt obtained thus, by crystallization from water, was dissolved in boiling alcohol (98 per cent.). The fact that it dissolved completely, giving a clear solution even after cooling, showed that it was free from lead sulphate. The alcoholic solution was evaporated to dryness and the product again recrystallized from water. So obtained, it gave the following results for water and lead :

.1456 gram of salt gave, at 160°, .0118 gram of water.

.17552 gram of salt gave, at 160°, .01432 gram of water.

.18031 gram of salt gave, at 160°, .08198 gram of lead sulphate.

.2091 gram of salt gave, at 160°, .09505 gram of lead sulphate.

$$\text{For Pb}\left(C_6H_3 \overset{\diagup CH_3}{\underset{\diagdown OCH_3}{-SO_3}} \right)_2 . 3H_2O.$$

	Theory.	Found.
H_2O	8.15	8.10–8.16
Pb	31.16	31.03–31.02

This lead salt, heated on platinum foil, first melts and then burns brilliantly, almost explosively, leaving a residue of carbon which finally burns away, leaving only a black stain on the platinum.

An attempt was made to make the silver salt by dissolving silver oxide in a hot solution of the acid. The salt is obtained in this way, but decomposes easily on boiling or on evaporation over a water-bath, giving a deposit of silver oxide. It was, therefore, not obtained in a pure condition. It was shown to crystallize in needles like the other salts, and to resemble them in its solubility in water and alcohol.

The sodium salt, though not purified, was shown to resemble the other salts in solubility and in its manner of crystallization.

Preparation of Paramethoxymetatoluenesulphonamide.

The amide obtained in the usual way was dissolved in alcohol (92 per cent.), and the solution boiled with animal charcoal, filtered, and evaporated to dryness. The second crystallization from water gave pure white needles, melting at 180°–181°. In

one experiment 18.5 grams of the diazo compound were boiled, under a pressure of 450 mm. of mercury, with 300 cc. of methyl alcohol (distilling at 65°–66°). The yield of purified amide was 4.9 grams, about 26 per cent. of the theoretical. The amide is but very slightly soluble in cold water, and dissolves with difficulty in boiling water. Approximate determinations showed that a liter of water at 10° dissolved about .8 gram of the amide. A liter of boiling water dissolves about 6 grams. The amide is moderately soluble in cold alcohol and ether. The following analyses show the composition of the substance to be $C_8H_{11}O_3NS$:

.27962 gram of the amide gave ammonia equivalent to 13.16 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter.

.2054 gram of the amide gave .23435 gram of barium sulphate.

.2669 gram of the amide gave .30085 gram of barium sulphate.

.24107 gram of the amide gave .42386 gram of carbon dioxide and .12190 of water.

$$\text{For } C_6H_3\text{---}SO_2NH_2. \begin{array}{c} \diagup CH_3 \\ \diagdown O\,CH_3 \end{array}$$

		Theory.	Found.
C_8	96	47.76	47.95
H_{11}	11	5.47	5.62
O_3	48	23.88	...
N	14	6.97	6.91
S	32	15.92	15.59 (15.50–15.69)
	201	100.00	

The sulphur determinations were made by Pearson's method, which, as before stated, is liable to give low results.

Besides this methoxy amide there was obtained, by working over the mother-liquors, a small quantity of impure metatoluenesulphonamide. It melted gradually at 94°–108°. It contained the small rhombohedral scales with iridescent reflection so characteristic of this amide. The yield was very small, less than one-tenth of a gram to 4.9 grams of the methoxy amide. The principal reaction with the diazo compound is evidently that in which the nitrogen is replaced by the methoxy group.

### Oxidation of Paramethoxymetatoluenesulphonamide.

Four grams of the amide and 1.3 grams of caustic potash, dissolved in 315 cc. of water, were treated with 6.5 grams of potassium

permanganate dissolved in the same amount of water. The mixture was heated on the water-bath about one and a half hours, when the decolorization of the potassium permanganate was complete. The solution was filtered and allowed to cool, when a little over one gram of the unchanged amide crystallized out. The solution, after filtering, contained the potassium salt of the oxidation-product, together with a small amount of the original amide. It was evaporated to a small bulk, and the small amount of amide which crystallized out was separated by filtration. The solution was then diluted to about one half a liter and acidified with hydrochloric acid. The white crystalline precipitate that was obtained was very slightly soluble in cold water, soluble with difficulty in much boiling water. It dissolves easily in cold alcohol. The second recrystallization from water gave a beautiful mass of needles which had all the appearance of a pure substance. It melted, however, with decomposition at 240°–270°. Nitrogen and sulphur determinations also showed plainly that the product was still impure. They differed .3 per cent. and .8 per cent. from the theoretical amount for $C_6H_3\overset{\displaystyle\diagup COOH}{\underset{\displaystyle\diagdown O.CH_3(p)}{-SO_2NH_2(m)}}$. They leave little doubt, however, as to the composition of the substance.

Barium Salt.—This salt is quite soluble in water, and crystallizes from a concentrated solution in clusters of pure white needles. It is nearly insoluble in strong alcohol. It was purified by boiling with alcohol (92-per cent.), filtering, and washing thoroughly with cold alcohol. Analyses showed the composition to be

$$Ba\left(C_6H_3\overset{\displaystyle\diagup CO_2}{\underset{\displaystyle\diagdown O.CH_3}{-SO_2NH_2}}\right)_2.3H_2O.$$

.1508 gram of the salt gave, at 250°, .01209 gram of water and .0541 gram of barium sulphate. This gives, for the percentage of water, 8.02; theory, 8.29; and for the percentage of barium, 21.03; theory, 21.04.

	Theory.	Found.
H_2O	8.29	8.02
Ba	21.04	21.03

The last molecule of water of crystallization was given off only by long heating at high temperatures. Without this last molecule

the salt was excessively hygroscopic, so that it was very difficult to get an accurate weight.

The attempt was made to get the pure acid by precipitating it from the barium salt with hydrochloric acid. The specimen obtained in this way was probably pure, but it still melted with decomposition at 240°–270°. It will be remembered that the corresponding ethoxy acid, although pure, behaved in a similar way. No further analysis was made of the acid, as the material was needed for other experiments.

Action of Propyl Alcohol on Paradiazometatoluenesulphonic Acid.

It appears, from what has been said, that when the diazo compound under consideration—$C_6H_3\overset{\diagup CH_3}{\underset{\diagdown N_2(p)}{-SO_2(m)}}$—is boiled under pressure with methyl or ethyl alcohol, the principal reaction that takes place is that in which the diazo group is replaced by the alkoxy group. It was thought of interest to determine whether the analogous reactions could be obtained with other alcohols. The action of propyl alcohol was tried and gave similar results.

Seventeen grams of the diazo compound were boiled with 250 cc. of propyl alcohol under a pressure of 200–220 mm. of mercury for about twenty minutes. The diazo compound was completely dissolved, giving a dark red solution, much darker than that obtained with the methyl or ethyl alcohol. The solution was neutralized with dry sodium carbonate and evaporated to dryness on a water-bath. A dark, gummy mass was left, which did not harden after long drying at 110° in an air-bath. On cooling, however, the mass became hard and could be pulverized. To the pulverized material was added an equal weight of phosphorus pentachloride. This gave a dark brown, gummy oil. By washing and treating with concentrated ammonia in the usual way, the crude amide was obtained in the form of a dark brown mass. This was washed with water and dissolved in alcohol. Boiling with animal charcoal failed to lighten the dark red color of the alcoholic solution. The solution was evaporated to dryness and the residue dissolved, boiled with animal charcoal, and recrystallized from water five times. In this way 1.6 grams of the pure white material were obtained. The melting-point was 126.5°–128°. The substance is nearly insoluble in cold water, moderately

soluble in boiling water, easily soluble in alcohol. It crystallizes in needles.

The following analyses show the composition of the substance to be $C_{10}H_{15}O_3NS$:

.19488 gram of the amide gave ammonia equivalent to 7.99 cc. of a standard ammonia solution containing 1.4672 grams of nitrogen to the liter.

.1337 gram of the amide gave .13397 gram of barium sulphate.

.26792 gram of the amide gave .5139 gram of carbon dioxide. The water was lost.

		For $C_{10}H_{15}O_3NS$.	
---	---	Theory.	Found.
C_{10}	120	52.40	52.31
H_{15}	15	6.55	...
O_3	48	20.96	...
N	14	6.11	6.02
S	32	13.97	13.97
	229	99.99	

Besides the propoxy amide a very small quantity of a substance having a low melting-point was obtained from the last mother-liquors. The amount was too small to admit of purification. It did not crystallize like the ordinary metatoluenesulphonamide, but in all probability it contained this compound. It was undoubtedly produced in less quantity than the propoxy compound. The yield of the latter, however, as has been seen, was very small, 17 grams of the diazo compound giving only 1.6 grams of the purified amide, or about 7.8 per cent. of theoretical. It is to be remembered that the actual yield was several times greater than this, loss being inevitable in repeated crystallizations of small amounts.

Pressure Experiments.

The experiments described above show that when paradiazo-metatoluenesulphonic acid is decomposed with methyl, ethyl, or propyl alcohol under a pressure of 200 mm. or more, the diazo group is replaced by the alcoholic group to a much greater extent than by hydrogen. Some experiments were performed in order to get an insight into the question of what influence, if any, pressure exerts on the course of the reaction. Time and material were lacking for an exhaustive study of this question, but the few preliminary experiments performed have some value.

Three lots of the diazo compound, of ten grams each, were treated in exactly the same way, with the one exception that one was decomposed at 200, the second at 400, the third at 600 mm. pressure. The ten grams were placed in the dry pressure-flask and 250 cc. of absolute methyl alcohol were added. The alcohol was then boiled, under pressure, for thirty minutes. Nitrogen was freely given off and the diazo compound was dissolved, giving a clear solution of an orange-yellow color. This was poured from the flask without rinsing, neutralized with 4.9 grams of dry sodium carbonate, and evaporated to dryness on a water-bath. About 11 grams of the pinkish white sodium salt were obtained. After cooling, 11 grams of phosphorus pentachloride were added. A red oil was thus obtained which, on cooling, solidified less perfectly than in some previous experiments. This chloride was washed in 1⅓ liters of cold water, each of the three lots being treated in exactly the same way. The same quantity of concentrated ammonium hydrate was then added to each. The material was allowed to stand in contact with the ammonia solution over night and then evaporated to dryness on a water-bath. The three lots of crude amide so obtained were boiled in the same quantity of distilled water. Each left a small residue of tarry matter. They were filtered through filter-papers of the same size, boiled with the same amount of animal charcoal, and again filtered through the same filters. The dishes and filters were rinsed with the same amount of boiling water. On cooling, a fairly pure specimen of methoxyamide was deposited in each case. That which had been decomposed at 200 mm. pressure and 71°–72° temperature gave 1.145 grams of the amide, or 11.28 per cent. of theoretical; that decomposed at 400 mm. pressure and 75°–76° temperature gave 1.325 grams of the amide, or 13.05 per cent.; that decomposed at 600 mm. pressure and 81° temperature gave 1.51 grams of the amide, or 14.88 per cent. The pressures were not kept perfectly constant but varied occasionally as much as 10 mm. each side of the figures given.

The amounts obtained do not represent the entire yield, as the mother-liquors were not worked over and the animal charcoal was not boiled to dissolve out the amide clinging to it. The mother-liquors and the animal charcoal were afterwards put together and from them a considerable additional quantity of the amide obtained. The figures given above, however, must represent very

closely the relative yield in each case, since the loss in each case must have been very nearly identical. The experiments show that an increase of pressure increases the yield of the methoxy compound.[1]

Some experiments, tried in essentially the same way with absolutely anhydrous ethyl alcohol, proved less satisfactory. The alcohol used was shown both by its method of formation, by its specific gravity, and by analysis to be entirely pure anhydrous alcohol. The odor of aldehyde was strong during each of the three experiments, and the relative yield of the ethoxy amide was so small, and the substance so mixed with the metatoluenesulphonamide and with an oily substance, that it proved impossible to separate it in such a way as to obtain any definite results. The appearance of the material indicated that the lot boiled at 600 mm. contained a considerably larger amount of the ethoxy compound than the others.

VI.—THE ACTION OF METHYL ALCOHOL ON PARADIAZO-
ORTHOTOLUENESULPHONIC ACID.[2]

By R. M. PARKS.

Comparatively few experiments have been made on the decomposition of diazo compounds by methyl alcohol, and these indicate that the decomposition generally yields the methoxy product. Hofmann[3] observed that the diazo compound obtained from amidine yields the methyl ether of trimethylbenzene. He also obtained anisol from diazobenzene and methyl alcohol. Griess[4] has shown that meta- and paradiazobenzoic acids give respectively metamethoxy- and paramethoxybenzoic acids, while the ortho acid gives benzoic acid. Metcalf[5] has shown that with methyl alcohol, paradiazometatoluenesulphonic acid yields mainly the corresponding methoxytoluenesulphonic acid.

Hayduck,[6] in decomposing the diazo compound of orthoamido-paratoluenesulphonic acid with methyl alcohol, obtained at ordinary pressure the methoxy product, namely, orthomethoxypara-toluenesulphonic acid, or, as Hayduck named it, methylcresolsulphonic acid.

[1] See Remsen and Dashiell: This Journal **15**, 105.

[2] From the author's thesis for the degree of Doctor of Philosophy. Presented to the Board of University Studies of the Johns Hopkins University, June, 1892.

[3] Ber. d. chem. Ges. **17**, 1917. [4] *Ibid.* **21**, 978.

[5] See preceding article. [6] Ann. Chem. (Liebig) **172**, 217.

Limpricht and Heffter,[1] from the diazo compound derived from paraamidoorthotoluenesulphinic acid and methyl alcohol, obtained paramethoxyorthotoluenesulphonic acid. This acid is apparently identical with the acid obtained in this investigation, and they are compared in the succeeding pages. The formulas of the amido acids from which the diazo compounds were derived are given here. The last is of the one used in this investigation, which I have undertaken at the suggestion and carried on under the direction of Professor Remsen.

Hayduck.   Metcalf.   Heffter.
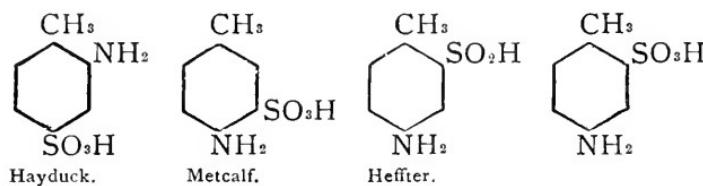
The paratoluidineorthosulphonic acid used in the experiments to be described was prepared according to the directions of Beilstein and Kuhlberg,[2] and of Brackett and Hayes.[3] From this the diazo compound was prepared according to the directions given by de Roode.[4]

Decomposition of the Diazo Compound with Methyl Alcohol.

A preliminary experiment at ordinary pressure was made and it was found that the diazo compound decomposed without difficulty. On evaporating the solution a dark heavy liquid having an acid reaction remained. This acid was converted into the barium salt by treatment with pure barium carbonate. On evaporation of the water solution there were deposited large tabular crystals together with a white powder. This result seemed to indicate the formation of two products, as in the decomposition with ethyl alcohol as described by Remsen and Dashiell.[5]

Three experiments were made under like conditions, that is, at ordinary pressure, with absolute methyl alcohol. In each case ten grams of the diazo compound were boiled with 200 cc. of absolute methyl alcohol in an Erlenmeyer flask connected with an inverted condenser. The decomposition began when the boiling of the alcohol commenced. That a decomposition was occurring was

[1] Ann. Chem. (Liebig) **221**, 344.   [2] Ann. Chem. (Liebig) **155**, 8.
[3] This Journal **9**, 399.   [4] This Journal **13**, 217.
[5] This Journal **8**, 105.

indicated by the change of color of the liquid and the escape of gas. The color was at first cherry-red, and at the end of the decomposition reddish brown. The reaction was complete in about one hour and fifteen minutes. By this time all solid matter had disappeared and the methyl alcohol simply boiled without the evolution of gas. Each portion was then connected with an ordinary condenser and the alcohol distilled from the product of decomposition. As in the preliminary experiment the acid residue was converted into the barium salt by means of pure barium carbonate. The water solution of the barium salt was evaporated to dryness and dried in the air-bath at 100°.

Experiment I. 10 grams of diazo compound gave 13.54
      "   II. 10   "   "   "   13.49
      "   III. 10   "   "   "   13.51
grams of barium salt.

The three portions were again dissolved in water and evaporated to crystallization. There first appeared a nearly white, not well crystallized salt, and then well crystallized, yellowish, sometimes reddish brown, tables. An attempt was made to separate the two salts by means of alcohol, as was done by Remsen and Dashiell,[1] but this did not prove satisfactory. In order to get material for immediate analysis, the well crystallized portion was separated mechanically from the white powder. The tabular crystals were first analyzed. The salt begins to lose water at 60°; at from 110° to 150° the weight is constant. The loss in weight corresponds closely to the loss of two molecules of water from the compound. On further heating to 165° the third and last molecule of water of crystallization was driven off, and higher heating did not produce any further loss. The analysis gave the following results:

I. 0.2530 gram of salt lost at 165° 0.0230 gram of water and gave 0.0990 gram of barium sulphate.

II. 0.2386 gram salt lost 0.0216 gram of water and gave 0.0937 gram of barium sulphate.

	Calculated for $\left(C_6H_3{-}SO_3^{<CH_3}_{<OCH_3} \right)_2 Ba.3H_2O.$	Found. I.	II.
H_2O	9.11	9.09	9.05
Ba	23.13	23.02	23.10

[1] *Loc. cit.*

Estimations of barium were now made both with the non-crystallized portion and also with the mixture of the well crystallized and non-crystallized which could not be separated mechanically. In the case of the white powder, or non-crystallized portion, it was not possible to determine water of crystallization. The results did not agree with each other. The analyses were made from the white powder and the mixture, after dehydrating at 165°, and gave the following results :

I. 0.2060 gram of the powder gave 0.0892 gram of barium sulphate.

II. 0.2399 gram of the powder gave 0.1043 gram of barium sulphate.

III. 0.2086 gram of the mixture gave 0.0896 gram of barium sulphate.

IV. 0.2541 gram of the mixture gave 0.1091 gram of barium sulphate.

If the hydrogen reaction had taken place at all, the barium salt of orthotoluenesulphonic acid should have been present. The comparison of the percentages of barium in the above four analyses with the percentage of barium in barium orthotoluenesulphonate and in barium paramethoxyorthotoluenesulphonate would give a strong indication as to the course of the reaction. The calculated percentages are for the anhydrous salts —

	Calculated for $\left(C_6H_4 {<}^{CH_3}_{SO_3} \right)_2 Ba.$	Calculated for $\left(C_6H_3 {-}^{CH_3}_{SO_3}{_{\searrow OCH_3}} \right)_2 Ba.$	I.	II.	III.	IV.
				Found.		
Ba	28.63	25.44	25.47	25.58	25.26	25.26

These analyses furnish no evidence that the hydrogen reaction had taken place. If it had occurred at all, it was to so small a degree as to escape detection by analysis. Further, in collecting the gas given off during the decomposition, no evidence could be obtained of the presence of formaldehyde. The gas was nitrogen only. The different portions which had been analyzed for barium with the results stated above were changed into the sodium salt. This sodium salt was treated with phosphorus pentachloride. The acid chloride thus formed was transformed into the amide by means of strong aqueous ammonia. There resulted only one amide melting at 150°. In fact all the derivatives and transformations subsequently made furnish additional evidence that there

was only one product formed. This product at ordinary pressure is paramethoxyorthotoluenesulphonic acid.

Experiment at Increased Pressure.

In order to study the influence of pressure on the course of the reaction, one experiment was made at an increased pressure of 200 millimeters and one experiment at a diminished pressure. The experiment at increased pressure was conducted in the apparatus used and described by Remsen and Dashiell.[1]

Ten grams of the diazo compound were decomposed with absolute methyl alcohol in the pressure-flask at 200 millimeters pressure. The same phenomena were observed as at ordinary pressure, only the decomposition was complete in about forty-five minutes. The barium salt made from the acid produced appeared like that formed from the product of decomposition at ordinary pressure. Analyses were made of the barium salt dehydrated at 165°, no attempt being made at separation. The results of analysis are as follows:

I. 0.1870 gram of substance gave 0.0809 gram of barium sulphate.

II. 0.2153 gram of substance gave 0.0928 gram of barium sulphate.

	Calculated for $\left(C_6H_3{\Large<}^{CH_3}_{OCH_3}SO_3\right)_2 Ba.$	I. Found.	II.
Ba	25.44	25.44	25.36

The only product of the reaction is therefore methoxytoluenesulphonic acid.

Experiment at Diminished Pressure.

An experiment was made at one-half atmosphere pressure also. The apparatus consisted of a strong one-liter balloon flask fitted with a three-hole rubber stopper. In one hole was a bent glass tube connected with a vacuum-gauge. Through the second ran a thermometer. The tube of an upright condenser passed through the third hole. Into the upper end of the condenser was fastened, by means of a one-hole rubber stopper, the short arm of a twice-bent glass tube, the long arm of which terminated a few millimeters below a two-hole rubber stopper in a filtering flask. A test-tube

[1] *Loc. cit.*

was placed upright within the flask, the open end being immediately below around the end of the long arm of the tube connected with the condenser. This tube served to collect the methyl alcohol should any distil over during the experiment. Through the second hole of the stopper in the filtering flask passed a bent glass tube, one end terminating in the bottom of the flask, the other end connected with a Bunsen suction-pump. By this means, if water should be drawn into the flask from the pump, it would not interfere with the experiment, and on admitting air into the apparatus the tube terminating in the bottom would conduct the water off completely. The pressure inside the apparatus was regulated by attaching a rubber tube to the side tube of the filtering flask and closing the rubber tube with a Mohr pinchcock. The pressure could then be regulated by hand. By carefully watching the vacuum-gauge or the thermometer the pressure could be kept constant for any length of time, *i. e.*, without a variation of more than 20 millimeters of pressure or 2° of temperature.

The diazo compound and absolute methyl alcohol were introduced into the flask, the pump turned on, and at one-half atmosphere pressure the flask was heated in a water-bath. The decomposition proceeded much more slowly than in previous experiments. The methyl alcohol boiled at 49°–51°, the pressure being about 380 millimeters.

Ten grams of diazo compound required six and one-half hours for complete decomposition. The methyl alcohol was distilled from the product of decomposition, barium carbonate added, and the barium salt evaporated to dryness, dehydrated, and analyzed for barium with the following results :

I. 0.1538 gram of the substance gave 0.0668 gram of barium sulphate.

II. 0.1933 gram of substance gave 0.0835 gram of barium sulphate.

	Calculated for $\left(C_6H_3{-}SO_3^{<CH_3}_{<OCH_3} \right)_2 Ba.$	Found.	
		I.	II.
Ba	25.44	25.55	25.41

As in the cases with ordinary and increased pressure, only one product could be obtained and this was the methoxy compound. Variation of pressure does not change the course of the reaction.

Paramethoxyorthotoluenesulphonic Acid.

In all subsequent experiments larger amounts of the diazo compound were decomposed with methyl alcohol. To one hundred grams of the diazo compound one liter of methyl alcohol was used. The product after distilling the methyl alcohol is a dark brown liquid easily soluble in alcohol and water. Made in large quantities it shows signs of crystallization after standing twenty-four hours. Set aside for several weeks it solidifies, but not in well-defined crystals. Boiling with animal charcoal does not entirely remove the color. After many attempts a small quantity of the acid was obtained in well-defined rhombohedral plates of a yellowish brown color. The acid decomposes without melting. The acid purified as far as possible with animal charcoal or the acid derived from the well-crystallized barium salt, was used for making salts.

Barium salt, $\left(C_6H_3 {-\!\!\!-} \genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown OCH_3}{-\!\!\!-} SO_3 \right)_2 Ba.3H_2O.$—Analyses of this salt have already been given. It crystallizes from concentrated water solution in large monoclinic tabular crystals with three molecules of water of crystallization. Only the well-crystallized is formed from the hot solution of thirty parts of salt in one hundred parts of water. If the concentration is greater than this the salt is first deposited from the hot solution in the form of a white powder having less than three molecules of water of crystallization. Since the crystals begin to lose water at 60° (also by standing in the air at ordinary temperature), it appears that even in boiling water at a certain concentration the salt loses some of its water of crystallization, probably two molecules. The salt is easily soluble in water, difficultly soluble in alcohol.

Calcium salt, $\left(C_6H_3 {-\!\!\!-} \genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown OCH_3}{-\!\!\!-} SO_3 \right)_2 Ca.4H_2O.$—This salt, prepared by neutralization of the free acid with finely powdered calcite, is exceedingly soluble in water, less so in alcohol. From water it forms a compact mass of lustrous, transparent crystals. Analysis for calcium and water gave the following results:

I. 0.2755 gram of the salt lost at 170° 0.0383 gram of water and gave 0.0726 gram of calcium sulphate.

II. 0.2402 gram of the substance lost 0.0335 gram of water and gave 0.0617 gram of calcium sulphate.

	Calculated for $\left(C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown OCH_3}{-SO_5}}}\right)Ca.4H_2O.$	Found. I.	II.
H_2O	14.01	13.90	13.94
Ca	7.78	7.77	7.58

Magnesium salt, $\left(C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown OCH_3}{-SO_3}}}\right)_2 Mg.5H_2O.$—This salt, prepared by neutralization of the free acid with pure magnesium carbonate, is very soluble in water and in alcohol. From water it crystallizes in radial tufts of short slender prisms; from alcohol, in white plates. Analysis for magnesium and water gave the following results:

I. 0.3192 gram of the salt lost at 140° 0.0545 gram of water and gave 0.0769 gram of magnesium sulphate.

II. 0.2174 gram of substance lost 0.0376 gram of water and gave 0.0495 gram of magnesium sulphate.

	Calculated for $\left(C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown OCH_3}{-SO_3}}}\right)_2 Mg.5H_2O.$	Found. I.	II.
H_2O	17.44	17.07	17.30
Mg	4.65	4.81	4.55

Zinc salt, $\left(C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown OCH_3}{-SO_3}}}\right)_2 Zn.6H_2O.$ — This is prepared by neutralization of the free acid with pure zinc carbonate. The salt is easily soluble in alcohol and in water; crystallizes in short, pointed prisms. Analysis for zinc and water gave the following results:

I. 0.2491 gram of salt lost at 165° 0.0466 gram of water and gave 0.0344 gram of zinc oxide.

II. 0.2791 gram of substance lost 0.0526 gram of water and gave 0.0387 gram of zinc oxide.

	Calculated for $\left(C_6H_3{\overset{\diagup CH_3}{\underset{\diagdown OCH_3}{-SO_3}}}\right)_2 Zn.6H_2O.$	Found. I.	II.
H_2O	18.77	18.71	18.85
Zn	11.34	11.09	11.14

Sodium salt, C_6H_3—$\begin{smallmatrix}\diagup CH_3 \\ SO_3Na.1\tfrac{1}{2}H_2O. \\ \diagdown OCH_3\end{smallmatrix}$—This is prepared by exact precipitation of the metal from the barium salt with a solution of sodium carbonate. It is extremely soluble in water and in alcohol. When evaporated almost to dryness, the solution, on cooling, solidifies to a compact mass of almost colorless leaflets. Analysis gave the following results:

I. 0.2844 gram of salt lost at 160° 0.0304 gram of water and gave 0.0811 gram of sodium sulphate.

II. 0.2863 gram of substance lost 0.0303 gram of water and gave 0.0820 gram of sodium sulphate.

	Calculated for C_6H_3—$\begin{smallmatrix}\diagup CH_3 \\ SO_3Na.1\tfrac{1}{2}H_2O. \\ \diagdown OCH_3\end{smallmatrix}$	Found. I.	II.
H_2O	10.75	10.69	10.58
Na	9.18	9.25	9.29

Potassium salt, C_6H_3—$\begin{smallmatrix}\diagup CH_3 \\ SO_3K.H_2O. \\ \diagdown OCH_3\end{smallmatrix}$—This is prepared by exact precipitation of the metal from the barium salt by a solution of potassium carbonate. It is very soluble in water and in alcohol. From the hot concentrated solution there is deposited a mass of almost colorless, fine branching needles. Analysis for potassium and water gave the following results:

I. 0.2297 gram of the salt lost 0.0160 gram of water and gave 0.0771 gram of potassium sulphate.

II. 0.2319 gram of substance lost 0.0165 gram of water and gave 0.0777 gram of potassium sulphate.

	Calculated for C_6H_3—$\begin{smallmatrix}\diagup CH_3 \\ SO_3K.H_2O. \\ \diagdown OCH_3\end{smallmatrix}$	Found.	
H_2O	6.97	6.97	7.12
K	15.11	15.07	15.04

Paramethoxyorthotoluenesulphonic chloride, C_6H_3—$\begin{smallmatrix}\diagup CH_3 \ (1) \\ SO_2Cl \ (2). \\ \diagdown OCH_3 \ (4)\end{smallmatrix}$—To the dried and powdered sodium salt a slight excess by weight of phosphorus pentachloride was added. The reaction soon began and proceeded with violence and with evolution of consid-

erable heat. Most of the phosphorus oxychloride was driven off by the heat of the reaction. The last portions of the oxychloride, held back by the sodium chloride, could not be entirely removed even when heated to 120°. After cooling the acid chloride was poured into a large amount of cold water and washed. The chloride is a heavy oil, yellowish white in color, very soluble in ether, from which it was not obtained in crystalline form, but reappeared as an oil after the slow evaporation of the ether.

Paramethoxyorthotoluenesulphonamide, C_6H_3 $\diagup CH_3$ $\diagdown OCH_3$ $—SO_2NH_2$.—This was prepared by treating the acid chloride with strong aqueous ammonia. The reaction began at once, the aqueous ammonia soon began to boil vigorously, and after shaking for a short time the amide suddenly solidified into a grayish white mass. After evaporating off the excess of ammonia on the water-bath and acidifying with hydrochloric acid, the amide was filtered and washed with cold water. The amide is very soluble in alcohol, in which it is best dissolved and decolorized with animal charcoal. It is then deposited from the hot concentrated alcoholic solution as white plates. The amide is difficultly soluble in cold and in hot water. From boiling water it crystallizes in quadratic plates if rapidly cooled ; if slowly, in short, pointed prisms with a vitreous lustre. The amide is soluble in ammonia and in the alkaline carbonates, from which it is precipitated on addition of acids. The pure amide melts at 151°. Not a trace of the amide of orthotoluenesulphonic acid was obtained from the mother-liquors. Analysis for sulphur and nitrogen gave the following results :

I. 0.3471 gram of the amide gave 0.4044 gram of barium sulphate.

II. 0.3177 gram of the amide gave 0.3720 gram of barium sulphate.

III and IV. Determinations of nitrogen (Kjeldahl).

	Calculated for $C_6H_3—SO_2NH_2$. $\diagup CH_3$ $\diagdown OCH_3$	Found. I.	II.
S	15.94	16.01	16.09
		III.	IV.
N	6.98	6.79	6.90

Comparison with the Oxymethyltoluenesulphonic Acid of Limpricht and Heffter.[1]

Heffter, when studying paraamidotolueneorthothiosulphonic acid, had changed this thiosulphonic acid into the corresponding sulphinic acid. On diazotizing the paraamidoorthotoluenesulphinic acid, and decomposing the diazo compound in absolute methyl alcohol, he obtained a non-crystallizing acid which he called oxymethyltoluenesulphonic acid. To this he gave the formula C_6H_3—SO_3H $\begin{smallmatrix}\diagup CH_3 & (1). \\ & (2). \\ \diagdown OCH_3 & (4)\end{smallmatrix}$ This acid is apparently identical with the product described above. As Heffter's description of the acid, its barium and potassium salts, did not agree in all particulars with the description of compounds of like composition and constitution already given in this article, it was thought advisable to repeat his experiments for the purpose of comparison. The starting-point of Heffter's experiments was paranitroorthotoluenesulphonic acid. The chloride of this acid, made by treating the potassium salt with phosphorus pentachloride and crystallizing from ether, when treated with acid ammonium sulphide passes over into the ammonium salt of paraamidoorthotoluenethiosulphonic acid, according to the equation:

$$C_7H_6\diagdown{}^{NO_2}_{SO_2Cl} + 4NH_4HS =$$
$$C_7H_6\diagdown{}^{NH_2}_{SO_2SNH_4} + NH_4Cl + 2NH_3 + 2H_2O + 3S.$$
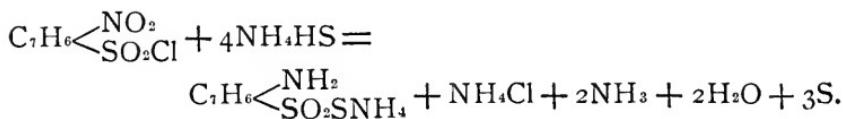
After concentration of the liquid and removal of the separated sulphur, the difficultly-soluble free thiosulphonic acid is precipitated by acetic acid.

This reaction was performed and the acid obtained as described, in hard, yellowish prisms. The change to the sulphinic acid is effected by boiling with hydrochloric acid or by means of sodium amalgam. Heffter advises the use of sodium amalgam. Therefore fifteen grams of the sodium salt of the thiosulphonic acid were reduced by about 600 grams of sodium amalgam, made by bringing together 600 grams of mercury and 20 grams of metallic sodium. By this reduction the sulphur of the group SH is

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[1] Ann. Chem. (Liebig) **221**, 344.

changed to hydrogen sulphide. Addition of acetic acid precipi-

tated the sulphinic acid $C_6H_3\underset{\diagdown NH_2 \ \ (4)}{\overset{\diagup CH_3 \ \ (1)}{-SO_2H \ \ (2)}}$.
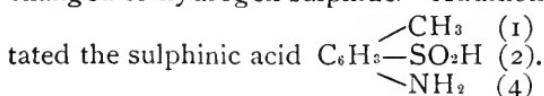
Crystallized from hot water the acid was obtained in colorless, hard prisms. The diazo compound of the sulphinic acid was made by Heffter, by passing nitrous acid into well-cooled absolute alcohol in which the finely divided sulphinic acid was suspended. The diazo compound forms yellow to brown needles, which are soon colored dark in the air. Water and alkalies decompose it at ordinary temperatures, with separation of a brown resin insoluble in alcohol and in ether. Some of the acid was suspended in absolute methyl alcohol, well cooled; then nitrous fumes were passed through. The diazo compound appeared in a short time as brown needles. These were quickly filtered and washed a few times with methyl alcohol. The diazo compound was then placed in a flask with methyl alcohol; the reaction proceeded at ordinary temperature. On warming on the water-bath the reaction was complete in a short time. Water was added, the precipitated mass filtered off, and the filtrate evaporated on the water-bath. Barium carbonate was then added, the barium salt filtered from the excess of barium carbonate and evaporated to dryness. A portion of the dried salt was dissolved in absolute alcohol by boiling. After cooling, addition of ether precipitated the salt as a yellowish powder, as described by Heffter. So far the work of Heffter was repeated.

Efforts were now made to obtain the salt in crystallized form by crystallizing from water. The dried barium salt, also the portion precipitated by ether from the alcoholic solution, were dissolved in water and boiled with animal charcoal. After filtering, the solution of the salt was bright yellow in color. It was evaporated to crystallization. On cooling of the concentrated solution there first appeared a white powder, then well-defined crystals like the barium salt described at the beginning of this article. The yield of barium salt was very small, twelve grams of the sulphinic acid giving but little more than one gram of the barium salt of the methoxy acid. Heffter says that eight grams of the sulphinic acid gave only one gram of the pure barium salt of the ethoxy acid, while the yield of the methoxy salt was still smaller. One analysis was made for barium and water, and one for barium only, in the dehydrated salt.

I. 0.2588 gram of the salt lost at 165° 0.0232 gram of water and gave 0.1036 gram of barium sulphate.

II. 0.2739 gram of dehydrated salt gave 0.1202 gram of barium sulphate.

	Calculated for $\left(C_6H_3{-}{\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{SO_3}}}\right)_2 Ba.3H_2O.$	Found. I.	II.
H_2O	9.11	8.96	...
Ba	23.13	23.55	...
Dehydrated salt:			
Ba	25.44	25.87	25.89

The differences are now narrowed down to the crystallizing power of the acid. But it must be said that only when working with large quantities of the acid is it possible to detect any signs of crystallization. As Limpricht and Heflter worked only with a very small quantity of the acid, it is not surprising that it was not obtained crystallized.

The conclusion seems to be justified that the two methoxy acids are identical. Whether the diazo compounds from which the acids are derived are identical or not is a question to which an answer is not attempted at this time.

Action of Potassium Permanganate on Paramethoxyorthotoluene-sulphonamide.

10 grams of paramethoxyorthotoluenesulphonamide, 40 grams of potassium permanganate with one liter of water were placed in a one and one-half liter flask, sunk in water and heated for some hours at the boiling temperature of water. The color of the permanganate disappeared in about three hours. The solution was then filtered from the insoluble manganese compounds and evaporated to a small volume. Addition of hydrochloric acid produced a white precipitate of fine needles. After filtering and washing the precipitate in cold water it was dissolved in boiling alcohol. The compound is easily soluble in hot alcohol, difficultly in cold. Any unoxidized amide is thus easily separated, as it is quite soluble in cold alcohol. From alcohol the methoxybenzoic sulphinide crystallizes in beautiful long, blade-like crystals, difficultly soluble in boiling water. On cooling of the water solution, long slender needles four to six centimeters in length appear. The crystals melt at 271°.

Analyses for sulphur and nitrogen show the compound to be paramethoxybenzoic sulphinide. The following are the results of analysis:

I. 0.1654 gram of the substance gave 0.1806 gram of barium sulphate.

II. 0.1833 gram of the substance gave 0.2025 gram of barium sulphate.

III and IV. Determinations of nitrogen after Kjeldahl (Gunning modification).

	Calculated for $C_6H_3{-}SO_2NH.$ with CO and OCH_3	Found.	
		I.	II.
S	15.04	15.00	15.18
		III.	IV.
N	6.59	6.47	6.74

Barium salt of methoxybenzoic sulphinide,

$\left(C_6H_3{-}SO_2N \genfrac{}{}{0pt}{}{CO}{OCH_3} \right)_2 Ba.3H_2O.$—Two grams of methoxybenzoic sulphinide were dissolved in boiling water and pure barium carbonate added. After boiling some time the excess of barium carbonate was filtered off and the filtrate evaporated to a small volume. The salt is easily soluble in water, from which it crystallizes in long colorless needles concentrically arranged. The air-dried salt was washed with absolute alcohol, recrystallized from water, and analyzed for water of crystallization and barium with the following results:

I. 0.2438 gram of the salt lost 0.0215 gram of water and gave 0.0920 gram of barium sulphate.

II. 0.1860 gram of the substance lost 0.0166 gram of water and gave 0.0701 gram of barium sulphate.

	Calculated for $\left(C_6H_3{-}SO_2N \genfrac{}{}{0pt}{}{CO}{OCH_3} \right)_2 Ba.3H_2O.$	Found.	
		I.	II.
H_2O	8.78	8.82	8.92
Ba	22.29	22.19	22.17

Acid potassium salt of paramethoxyorthosulphobenzoic acid,

$C_6H_3{-}SO_2K.H_2O.$ with CO_2H and OCH_3—If the filtrate from methoxybenzoic sulphinide be evaporated almost to dryness, potassium chloride first crys-

tallizes, then long beautiful prisms, almost colorless, which proved to be the acid potassium salt of paramethoxyorthosulphobenzoic acid. The salt can be obtained from these mother-liquors either by fractional crystallization to free it from potassium chloride, or by evaporating to dryness and extracting with alcohol. The salt is much more soluble in alcohol than potassium chloride, and may thus be obtained quite pure. Analysis of the salt gave the following results :

I. 0.2628 gram of the salt lost at 125° 0.0166 gram of water and gave 0.0786 gram of potassium sulphate.

II. 0.2224 gram of dehydrated salt gave 0.0714 gram of potassium sulphate.

	Calculated for $C_6H_3{-}SO_3K.H_2O.$ $\diagup CO_2H$ $\diagdown OCH_3$	Found. I.	II.
H_2O	6.25	6.32	...
K	13.58	13.43	...
Dehydrated salt :			
K	14.44	...	14.41

The acid potassium salt was made also by oxidizing the potassium salt of paramethoxyorthotoluenesulphonic acid. Ten grams of this salt were dissolved in 1 liter of water, 15 grams of potassium permanganate added, and the solution heated in boiling water. The color of the permanganate disappeared in about two hours. After removing the insoluble manganese compounds and evaporating to a small volume, strong hydrochloric acid throws down the acid potassium methoxysulphobenzoate as short needles. These needles, recrystallized from water and analyzed, gave the following results :

I. 0.2766 gram of the salt lost 0.0174 gram of water and gave 0.0842 gram of potassium sulphate.

II. 0.2763 gram of dehydrated salt gave 0.0894 gram of potassium sulphate.

	Calculated for $C_6H_3{-}SO_3K.H_2O.$ $\diagup CO_2H$ $\diagdown OCH_3$	Found. I.	II.
H_2O	6.25	6.29	...
K	13.58	13.66	...
Dehydrated salt :			
K	14.44	...	14.49

Acid barium salt, $\left(C_6H_3{\overset{\nearrow CO_2H}{\underset{\searrow OCH_3}{-SO_3-}}} \right) Ba.4H_2O.$ — This was pre-
pared from the free methoxysulphobenzoic acid. A water solution
of the acid was divided into two equal parts; one part was neutral-
ized with barium carbonate. To this neutral barium salt the
second part of the acid was added to produce the acid salt. Both
the neutral and acid salts are extremely soluble in water and were
not obtained in crystals. In hydrochloric acid the acid barium
salt is difficultly soluble, and from it it crystallizes in fine white
needles. Analysis gave the following results:

0.2212 gram of the salt lost at 180° 0.0234 gram of water and
gave 0.0761 gram of barium sulphate.

	Calculated for $\left(C_6H_3{\overset{/CO_2H}{\underset{\backslash OCH_3}{-SO_3-}}} \right)_2 Ba.4H_2O.$	Found.
H$_2$O	10.72	10.58
Ba	20.44	20.24

Paramethoxyorthosulphobenzoic acid, $C_6H_3{\overset{\nearrow CO_2H\ (1)}{\underset{\searrow OCH_3\ (4)}{-SO_3H\ (2)}}}$.—This
acid was first prepared from the acid potassium salt by converting
the salt into the chloride by means of phosphorus pentachloride,
then decomposing the acid chloride in boiling water, evaporating
to dryness and recrystallizing from water. A second method is
to pass from the methoxybenzoic sulphinide to the acid. This is
accomplished by boiling the methoxybenzoic sulphinide in dilute
hydrochloric acid, one part of the concentrated acid to eight parts
of water. As in the case of benzoic sulphinide, the acid ammo-
nium salt of the corresponding acid is formed. The acid ammo-
nium salt when treated with twice its weight of phosphorus penta-
chloride gives the chloride. When this chloride is boiled with
water, hydrochloric acid is given off and the acid is formed. Crys-
tallized from water, in which it is quite soluble, this acid appears
as long, interlacing needles, transparent and colorless. It melts
without decomposition at 104°. On cooling it quickly solidifies,
and when again heated melts at the same point. This may be
repeated without change of the melting-point.

Chloride of paramethoxyorthosulphobenzoic acid, $C_6H_3{\overset{\nearrow COCl}{\underset{\searrow OCH_3}{-SO_2Cl.}}}$

—The chloride prepared as above described for the preparation

of the methoxysulphobenzoic acid is a white solid. It does not dissolve easily in ether. From ether it crystallizes in small, hard crystals, transparent and colorless. The crystals powdered and boiled with aqueous ammonia give the methoxybenzoic sulphinide melting at 271°.

Comparison of Paramethoxyorthosulphobenzoic Acid with the Sulphanisic Acid of Zervas.[1]

Anisic acid, $C_6H_4{<}^{COOH\ (1)}_{OCH_3\ (4)}$, according to the theory, should give two sulphonic acids, one with the sulphonic acid group in the ortho position to carboxyl, the other with this group in the meta position to carboxyl:

$$C_6H_3\begin{cases} COOH & (1) \\ SO_3H & (2) \\ OCH_3 & (4) \end{cases} \text{ and } C_6H_3\begin{cases} COOH & (1) \\ SO_3H & (3) \\ OCH_3 & (4) \end{cases}.$$
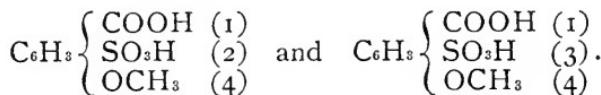
By derivation the acid described in this paper should be expressed by the first of these formulas. It was thought advisable to repeat the experiments as follows: 5 grams of crystallized anisic acid in a small Erlenmeyer flask were covered with fuming sulphuric acid and heated in a water-bath for two hours. After cooling, the contents of the flask were poured into cold water. This solution of sulphanisic acid and the excess of sulphuric acid was neutralized with pure lead carbonate. The lead salt as described by Zervas was found to crystallize from hot water in beautiful transparent crystals. It was transformed into the sodium salt by precipitation of the metal with a solution of sodium carbonate. A portion of this salt was fused with potassium hydroxide, and thus converted into protocatechuic acid, which was crystallized from ether. A portion of the crystals was dissolved in water, and this solution gave the characteristic color reaction with ferric chloride, namely, dark green. Addition of a very little sodium carbonate changed the green color to blue, passing rapidly into red. The melting-point of the needles from ether was found to be 194°.

Some of the methoxybenzoic sulphinide was fused with potassium hydroxide also. The products were resorcin and 1, 2, 4-dioxybenzoic acid. Both were recognized by their melting-

points and by the reaction with ferric chloride. It is therefore clear that the methoxy acid described in this article is not identical with the sulphanisic acid of Zervas, and that in the latter the sulphonic-acid group is in the meta position with reference to the carboxyl.

Summary.

I. When paradiazoorthotoluenesulphonic acid is decomposed with absolute methyl alcohol at ordinary, increased, or diminished pressure, only the methoxy product is formed, namely, para-methoxyorthotoluenesulphonic acid.

II. This result does not conform to the rules deduced from the study of the decomposition of diazo compounds with ethyl alcohol, but does confirm the suggestion that the simpler alcoholic group is introduced more easily than more complex ones.

III. The product of the reaction is identical with the oxy-methyltoluenesulphonic acid obtained by Limpricht and Heffter in the decomposition of the diazo compound from paraamido-orthotoluenesulphinic acid with methyl alcohol.

IV. When paramethoxyorthotoluenesulphonamide is oxidized by potassium permanganate, paramethoxybenzoic sulphinide is formed. From this can be obtained paramethoxyorthosulpho-benzoic acid.

V. Paramethoxyorthosulphobenzoic acid is isomeric with sulphanisic acid, and, when fused with potassium hydroxide, it gives resorcin and β-resorcylic acid are formed.

ON THE EXISTENCE OF DOUBLE SALTS IN SOLUTION.

By C. E. Linebarger.

If a solution of two salts be concentrated, they will pass from the dissolved into the solid state in one of four ways: (1) The salts may assume independently the solid state. If their solubilities be considerably different, one may pass almost completely out of solution before the other even commences to do so. Upon this fact is based the process of separation known as "fractional crys-

tallization." (2) The two salts may assume simultaneously the solid state, forming an isomorphous mixture. Two cases are to be distinguished : (*a*) the mixed crystals are miscible in all proportions; (*b*) one or the other of the component crystals is in excess. There may be a limited or an unlimited capability of mixture, just as liquids may be miscible in all proportions, as alcohol and water, or in limited proportions, as water and ether. (3) The crystals may separate out of the solution in definite stoichiometrical proportions. The crystalline compound may be a complex or a double salt, the criterion of a double salt being that it gives in aqueous solution the same reactions as its components. (4) The salts may form mixed crystals as well as double salts, but only within certain limits of concentration.

It is a debated question whether double salts exist as such in solution, or first come into being at the moment of crystallization. Yet much work has been done upon the subject, and from various points of view. Especially have experiments upon diffusion been performed, for the purpose of getting information as to the state of dissolved double salts. Graham[1] found that the constituent salts of certain double salts, as alum and the like, were present in the diffusate in different proportions from those in the double salt, as they diffused with different velocities ; a fact that indicates a partial decomposition, at least, of the double salts. On the other hand, his experiments with the double sulphates of copper and potash, and of magnesia and potash, led him to conclude that these double salts dissolve in water without decomposition. But, as Marignac remarks,[2] these last experiments are not conclusive, since it was ascertained merely that the weight of the diffused double salt was equal to the sum of the weights of the component salts when diffused separately, and not that the relative proportions of the constituents remained constant. This latter investigator states that his experiments on the diffusion of pairs of salts did not seem to indicate that there was any difference between the behavior of solutions containing salts which form solid double salts and that of solutions of salts incapable of combining with each other. Van der Wal[3] performed some experiments on the diffusion of various double salts which showed that they were decompounded in solution. Ingenhoes,[4] also, states that the double salts

[1] Phil. Mag. 1850, p. 1.
[3] Inaugural Dissertation. Leyden, 1869.
[2] Ann. chim. phys. [5] **2**, 546 (1874).
[4] Ber. d. chem. Ges. **12**, 1678 (1879).

investigated do not exist in solution, "for they diffuse like the separate salts." Rüdorff[1] concluded from diffusion-experiments that double salts, although generally dissociated when dissolved, yet, shortly before crystallization, come into being. Trevor,[2] however, on repeating with some modifications Rüdorff's experiments on the double sulphates of copper and potassium, found it probable that that double salt does not exist at all in solution.

The changes of volume that take place when solutions of salts are mixed have been interpreted so as to disprove the existence of double salts in solution. Kremers,[3] on mixing solutions of salts capable of forming a double salt, found the volume of the mixture to be approximately equal to the sum of the volumes of the component salt solutions before mixing, if these contained the salts in molecular proportions. He therefore assumed that the combination of the two single salts to form the double salt did not take place in solution. Similar conclusions based upon like experimental data were arrived at by Favre and Valson.[4]

Appeal has been made to thermochemistry for facts that may aid us in deciding whether double salts exist in solution or not. Every true chemical change being accompanied by some thermal manifestation, solutions of salts capable of forming a double salt should, when mixed, absorb or evolve heat, provided that the double salt is formed in the solution. Berthelot[5] found that heat was evolved on mixing solutions of the halogen salts of mercury and of the alkalies. A similar observation was made by Graham[6] in the case of solutions of the chlorides of mercury and ammonium. His experiments with some double sulphates, however, showed that no heat was evolved on mixing their solutions. Observations of a similar kind were made by Favre and Silbermann[7] as well as by Favre and Valson.[8]

Valuable information as to the condition of double salts in solution is to be got from the knowledge of the freezing-points and electrical conductivities of their solutions. Raoult[9] determined the lowering of the point of congelation of solutions of fourteen double salts. Of these, with the exception of such as are formed with evolution of heat, the freezing-points were lowered to a temperature corresponding to the sum of the lowerings of the freezing-points of

[1] Ber. d. chem. Ges. **21**, 4, 1882 (1888).
[2] Ztschr. phys. Chem. **7**, 468 (1891).
[3] Ann. der Phys. Pogg. **98**, 58 (1856).
[4] Compt. rend. **77**, 907 (1873).
[5] Ann. chim. phys. [5] **29**, 202 (1883).
[6] Phil. Mag. **24**, 401 (1844).
[7] *Loc. cit.*   [8] *Loc. cit.*
[9] Compt. rend. **99**, 914 (1884).

solutions of the constituent salts, which indicates that dissociation had taken place. The theory of solubility-effect teaches that in the case of two salts possessing a common ion, the addition of one to a saturated solution of the other occasions a precipitation, unless a double salt is formed. Le Blanc and Noyes,[1] in making an investigation of solutions of certain salts in which no precipitation was caused by the addition of one salt to a solution of the other, found that in fact double salts were formed in the solution. Kistiaskowsky,[2] in seeking experimental proof of the propriety of the distinction between complex and double salts, drawn by Ostwald,[3] ascertained that the double salts examined by means of the cryoscopic method were almost completely decomposed into their components. On the electrical conductivity of solutions of double salts, work has been done by Hittorf,[4] Grotrian,[5] Klein,[6] Kistiaskowsky,[7] Wershoven,[8] Bouty,[9] Le Blanc and Noyes,[10] and Chroustshoff and Pachkoff,[11] the general results of which indicate that in dilute solutions, double salts are considerably dissociated, while in concentrated solutions their dissociation is but slight; this is especially the case with such salts as contain a salt of mercury or of cadmium.

The study of double salts in dynamic equilibrium with their solutions is of importance for the question under consideration. The simultaneous solution of two salts has been the subject of numerous investigations, some of which have a bearing upon the question as to the possibility of the existence of double salts in solution. Mulder[12] found that when water is saturated with two salts, there is often a simple equivalent ratio between the dissolved salts, indicating the presence of a double salt in solution. Rüdorff,[13] observing that on adding to saturated solutions of double salts an excess of one of the components, a part of the other was deposited from the solution, criticizes the conclusions of Mulder and states that a formation of double salts in solution cannot be thought of. But Trevor[14] has proven Rüdorff's experiments to be incomplete, so that his conclusions cannot be said necessarily to follow. The thorough investigations of Roozeboom,[15] Meyerhoffer,[16] and

[1] Ztschr. phys. Chem. **6**, 398 (1890).   [2] *Ibid.* **6**, 97 (1890).   [3] *Ibid.* **3**, 600 (1889).
[4] Ann. der Phys. Pogg. **106**, 524 (1859).   [5] Ann. der Phys. Wied. **18**, 177 (1833).
[6] *Ibid.* **27**, 151 (1886).   [7] *Loc. cit.*   [8] Ztschr. phys. Chem. **5**, 481 (1890).
[9] Ann. chim. phys. [6] **14**, 78 (1888).   [10] *Loc. cit.*   [11] Compt. rend. **108**, 1162 (1889).
[12] Jsb. Chem. **1864**, 92, and **1866**, 65.   [13] Ann. der Phys. Pogg. **148**, 558 (1873).
[14] Ztschr. phys. Chem. **7**, 468 (1891).   [15] *Ibid.* **2**, 513 (1888).   [16] *Ibid.* **3**, 336 and **5**, 97.

Schreinemaker,[1] on the states of equilibrium of double salts with their solutions, show that the few double salts examined are capable of existence in concentrated solution within certain limits of concentration.

Bodländer[2] has shown, by means of determinations of the solubility of the molecular compound of ammonia and silver chloride, as well as of the freezing-points and electrical conductivity of its solutions, that it certainly exists in solution.

Fischer and Schmidner[3] determined the relative quantities of the components of double salts whose solutions had been drawn up by capillary attraction into rolls of filter-paper placed in a tube. Experiments carried out with double salts soluble in alcohol as well as in water, showed that while in aqueous solution a larger amount of the more diffusible component was taken up by the paper than of the less diffusible component, in alcoholic solution the ratio of the quantities of the components found in the paper was the same as that in the double salt. These facts show that water, but not alcohol, has the power of decompounding the double salts examined.

On comparing the results of the foregoing investigations we see that double salts, as regards their capability of existing in solution, may be divided into two groups. The first group embraces the double sulphates, the double halides of the alkalies and alkaline earths, and the like; the second group comprises the double halide salts of mercury or of cadmium with the alkalies. The members of the first group are almost completely decompounded in solution, as shown by experiments on the contractibility, diffusibility, electric conductivity and freezing-points of their solutions, as well as by the circumstance that no thermal change is manifested on mixing solutions of their component salts. One, at least, of the constituent salts crystallizes with water of crystallization, and both undergo electrical dissociation to a not inconsiderable degree. The members of the second group are but slightly decompounded in concentrated solutions, although on dilution they become more so. When solutions of their components are mixed, heat comes into play. Their freezing-points and electrical conductivities differ widely from the sums of those of their components. One, at least, of the simple salts does not crystallize with water of crystallization, and suffers merely a slight dissociation into its ions.

[1] Ztschr. phys. Chem. **9**, 57.   [2]*Ibid.* **9,** 730.   [3]Ann. Chem. (Liebig) **272**, 156 (1892).

All of the facts observed with regard to aqueous solutions of double salts can be satisfactorily accounted for by means of Arrhenius' electrochemical theory. The existence of double salts in solution depends upon the temperature and degree of dilution. Likewise the degree of electrical dissociation of salts depends upon the temperature and concentration. If solutions of salts which are almost completely dissociated into their ions be mixed, no evidence of a chemical action is apparent. This is also the case if the salts are capable of combining with each other to form a solid double salt. The undissociated portions of the salts may indeed unite to form the double salt, but the reaction is inappreciable, and the more so the greater the electrical dissociation. As the ions of the simple salts lead an independent existence in solution, no appreciable formation of a double salt occurs except in the moment of crystallization. The double salts of the first group correspond in a measure to these conditions. If, however, one of the constituents of a double salt suffer but a slight decomposition into its ions, it is found that solutions of the component salts, when mixed, give out heat, and that the physical properties of the solution vary with the concentration. Such phenomena are observed especially with solutions of double salts of the second group. As the "activity-coefficient" increases with dilution, the more dilute the solution the greater the proportion of electrically dissociated to undissociated molecules. The degree of dissociation into ions increases also with the temperature, so that for a given concentration there exists a temperature above which electrical dissociation is so nearly complete that no double salt can be said to exist. In answering, then, the question as to the existence of double salts in aqueous solution, we should first ascertain what is the state of the components at the given temperature and concentration. That known, we can compute what amount of double salt may be present as such in solution.

These considerations obtain only for aqueous solutions. The experiments of Fischer and Schmidner (*loc. cit.*) show that in alcohol, a liquid that exerts but little dissociative power, double salts are soluble without decomposition, at least at ordinary temperatures. It seemed desirable to extend such observations to other liquids and other double salts. I have accordingly made a study of solutions of certain double salts in several organic solvents, the results of which are given in this paper.

Of the pairs of salts examined, one of each pair was practically insoluble in the solvents employed. Solutions of the soluble salt were kept in contact with the insoluble salt at a constant temperature. The assumption made was that if any of the insoluble salt entered into solution, it would do so with formation of the double salt. Hence the quantities of the dissolved salts should be in stoichiometrical ratio, and, if that was found to be the case, the conclusion that the double salt exists as such in solution would be legitimate. The experiments were carried out as follows: An excess of the insoluble salt was added to a solution of the soluble salt, and the whole kept at a constant temperature, with frequent and thorough agitation. After 36–40 hours, samples of the solution were drawn off by means of a pipette, introduced into a small glass-stoppered flask, weighed, the solvent distilled off, and the residue analyzed.

Benzene, Mercuric Chloride and Sodium Chloride.

Benzene[1] was added to a large excess of mercuric[2] as well as of sodium[3] chloride, and the whole was digested at 40° for 48 hours. A portion of the solution was then removed and the benzene and corrosive sublimate determined.[4] Table I. records the results.

Table I.

Wt. of Sol.	Wt. of Benzene.	Wt. of Residue.	Wt. of $HgCl_2$.
13.473 grams.	13.361 grams.	0.112 gram.	0.1124 gram.

from which it is seen that no sodium chloride has entered into solution. The conclusion to be drawn is that any double salt of corrosive sublimate and common salt is incapable of existence in benzene solution.

Acetone,[5] Mercuric Chloride and Sodium Chloride.

Mercuric chloride reacts chemically upon acetone at ordinary temperatures, so that this system of substances does not admit of

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[1] The benzene had been carefully freed from thiophene by treatment with sulphuric acid. It was then repeatedly crystallized, and finally distilled over sodium.

[2] This was the commercial *c. p.* article and had been purified by a couple of crystallizations from water.

[3] Commercial *c. p.* sodium chloride was dissolved in water and precipitated by passing hydrochloric acid gas into the solution. The salt was ignited in a platinum dish to remove the last traces of moisture.

[4] The mercuric chloride was determined volumetrically by means of a standard solution of potassium iodide. The method gave very concordant results.

[5] Obtained by repeated fractional distillations of commercial article. It boiled at 56.4° at 757 mm. pressure.

a very accurate study. Still I have carried out some experiments with not too concentrated solutions at low temperatures, the results of which are given in Table II.

TABLE II.

Temperatures,	0°	0°	0°	0°	0°	5°	10°
Molecules of $HgCl_2$ to 100 mols. of $(CH_3)_2CO$	12.0	22.0	8.6	5.1	4.4	2.6	21.0
Molecules of NaCl to 100 mols. of $(CH_3)_2CO$	11.2	22.9	8.3	4.9	4.4	2.7	21.1

It is seen that the ratio of the number of molecules of the two salts is as 1 : 1, that is, a double salt consisting of one molecule of mercuric chloride and one molecule of sodium chloride is formed. On allowing a saturated solution of the two salts to evaporate I obtained a double salt crystallizing in long needles, the composition of which is represented by the formula $(HgCl_2)_2NaCl$. The salt $HgCl_2.NaCl$ I have as yet been unable to obtain from acetone solution. This is probably due to the different solubilities of the two double salts.

Acetic Ether,[1] *Mercuric Chloride and Sodium Chloride.*

When sodium chloride is added to solutions of mercuric chloride in acetic ether, it dissolves rapidly and, if it be in excess, the resulting solution always contains one molecule of common salt to two molecules of corrosive sublimate. The results of a series of determinations are given in Table III.

TABLE III.

Temperatures,	30°	33°	41.8°	42°	45°	48°
Mols. of $HgCl_2$ to 100 mols. $C_4H_8O_2$,	21.1	24.5	2.5	34.0	8.0	17.1
Mols. of NaCl to 100 mols. $C_4H_8O_2$,	10.7	12.2	1.2	17.0	4.1	8.4

This table shows that in acetic-ether solution a double salt with the composition represented by the formula $(HgCl_2)_2.NaCl$ is formed. That only this double salt is present in the solution is proven by the following experiments: The double salt $HgCl_2.NaCl.2H_2O$ (prepared by dissolving equal numbers of molecules

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[1] Carefully distilled fractionally over calcium chloride and finally over a little sodium. Boiling-point was 74.4° at 757 mm.

of the salts in water and recrystallizing from dilute alcohol) was carefully dehydrated at 100°, and a portion added to acetic ether. A precipitation of salt took place, and an analysis of the solution showed the two salts to be in the same proportions as in the double salt $(HgCl_2)_2.NaCl$, that is, a decomposition took place in accordance with the following equation :

$$2(HgCl_2.NaCl) = (HgCl_2)_2.NaCl + NaCl.$$

The results of a number of analyses of solutions obtained in this way are given in Table IV.

TABLE IV.

Temperatures,	15°	25°	30°	35°	40°
Mols. of $HgCl_2$ to 100 mols. $C_4H_8O_2$,	12.1	8.0	20.0	4.0	24.1
Mols. of NaCl to 100 mols. of $C_4H_8O_2$,	6.1	4.0	9.8	2.1	12.3

If sodium chloride dissolves in acetic-ether solution of mercuric chloride with formation of the double salt $(HgCl_2)_2.NaCl$, the number of dissolved molecules must remain unchanged. Now as the amount of the depression of the freezing-point as well as of the elevation of the boiling-point depends upon the number of dissolved molecules, the addition of common salt to a solution of corrosive sublimate in acetic ether ought not to alter the boiling- or freezing-point of that solution. This has been found to be true in the case of the boiling-point, a freezing-point determination naturally being impracticable with such a solvent as acetic ether. The temperature of a boiling solution of mercuric chloride in acetic ether was determined by means of the apparatus used in determining molecular weights, and, without the boiling being discontinued, small quantities of sodium chloride were added from time to time. It was impossible to detect any change in the boiling-point.

The preceding experiments show that the double salt $(HgCl_2)_2.$ NaCl exists in acetic ether solution at temperatures between 0° and 50°. At somewhat higher temperatures, however, the salt becomes decompounded. Thus, a solution of the double salt when heated to about 140° in a sealed tube deposits a portion of the salt.

Acetic Ether, Mercuric Chloride and Potassium Chloride.

Small quantities of potassium chloride were added from time to time to a saturated solution of mercuric chloride, the temperature being kept at 40°, and after equilibrium had established itself, a sample of the solution was removed and analyzed. Soon, however, a white flocky precipitate separated out, which had a composition corresponding to the formula $HgCl_2.KCl$. This double salt was also obtained by adding all at once one molecule of finely powdered potassium chloride to one molecule of mercuric chloride dissolved in considerably more acetic ether than necessary for saturation. After a few days nearly all the corrosive sublimate had been precipitated from solution. No double salt of these two salts seems capable of existence in acetic ether solution.

Acetic Ether, Mercuric Chloride and Lithium Chloride.

In Table V. are given the results of some determinations of the solubility of lithium chloride in solutions of mercuric chloride in acetic ether.

TABLE V.

Temperatures,	0°	10°	20°	30°	40°
Mols. $HgCl_2$ to 100 mols. $C_4H_8O_2$,	8.2	0.9	6.3	0.6	6.4
Mols. LiCl to 100 mols. $C_4H_8O_2$,	8.5	1.0	6.5	0.9	6.8

Here it is permitted to assume that the double salt $HgCl_2.LiCl$ is formed, the excess of lithium chloride over one molecule being due to its slight solubility.

Experiments of a qualitative nature were carried out with solutions of cadmium bromide and cadmium iodide in acetone as well as in acetic ether. It was found that the chlorides of potassium and sodium were quite freely soluble in such solutions, undoubtedly with formation of double salts.

A consideration of the foregoing experiments shows that the temperature and the nature of the solvent are of decided influence in determining the kind and stability of the double salts that may be formed in it. But little influence can be ascribed to the degree of dilution in the case of solvents which do not have any considerable electric dissociative power, although in aqueous solutions the concentration plays an important part. The number of double

salts studied above might be extended indefinitely. Of the greatest importance, however, would be the study of one system throughout a considerable range of temperature; accordingly, I am engaged in the investigation of the states of equilibrium of the system composed of the substances acetic ether, mercuric chloride and common salt, which seems admirably adapted for such work.

CHICAGO, ILL., *March* 22, 1893.

THE MOLECULAR WEIGHT OF HYDROGEN PEROXIDE AND OF BENZOYL PEROXIDE.

BY W. R. ORNDORFF AND JOHN WHITE.

Although hydrogen peroxide, because of its peculiar nature and its various applications in the arts and sciences, has been the subject of much study, it is only very recently that any attempt has been made to determine its molecular weight. This has without doubt been chiefly due to the ease with which the substance decomposes and the difficulty of obtaining perfectly pure solutions, also because, until the development of Raoult's Law and its application by Beckmann, no method was known by which its molecular weight could be determined.

Early investigators proved by analytical means that hydrogen peroxide contains double the amount of oxygen found in water, and expressed this by using the simplest formula in accordance with the facts: HO_2, or, with the present system of atomic weights, H_2O_2.

Tammann,[1] making use of the cryoscopic method of determining molecular weights, obtained results which led him to the conclusion that the formula for hydrogen peroxide is double that usually employed, *i. e.*, H_4O_4 instead of H_2O_2.

Such a conclusion would in itself be sufficiently startling, involving as it does a theory of linkage of the atoms in which oxygen

1 Ztschr. phys. Chem. **4**, 441.

is trivalent; but if in addition to this there be taken into consideration the peculiar nature of his experimental data and the methods by which the conclusion was deduced, it becomes apparent that the work needs confirmation. The authors of this paper, therefore, undertook a repetition of Tammann's work, and had already obtained results leading to a conclusion different from that deduced by him, when an article on the same subject by Carrara[1] appeared. Carrara made determinations of the molecular weight of hydrogen peroxide in aqueous solution, using the cryoscopic method, and also determined the coefficient of refraction of solutions of the substance. In both cases he obtained results which led to the conclusion that the correct formula for hydrogen peroxide is H_2O_2.

We have, then, two conclusions as to the molecular weight of hydrogen peroxide, both deduced from results obtained from the lowering of the freezing-point of its aqueous solution, one giving as its formula H_4O_4, the other H_2O_2. It may be stated here that the results of the authors' work, most of which was done before they had seen Carrara's article, lead to the same conclusion as that deduced by him, *viz.*, that the formula for hydrogen peroxide is H_2O_2.

In establishing this conclusion, they have determined not only the molecular weight of hydrogen peroxide, but also that of the most stable of the organic derivatives of hydrogen peroxide, *i. e.*, benzoyl peroxide, $(C_6H_5CO)_2O_2$, described by Brodie.[2]

Experimental.

Preparation of a pure solution of hydrogen peroxide.—For the purpose of obtaining a pure solution of hydrogen peroxide, the commercial solution, labeled pure and for medicinal purposes, was used as a starting-point, and the methods of purification were essentially those given by Hanriot.[3]

This solution was found to contain small amounts of the following substances: barium, calcium, sodium, aluminium, iron; hydrochloric, sulphuric and phosphoric acids; also a small amount of an insoluble substance which was found to consist chiefly of silica. To purify this solution a concentrated solution of barium hydroxide was added until it gave an alkaline reaction, this precipitated all

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[1] Gazz. chim. ital. (1892), **10**, 1.

[2] Proc. Roy. Soc. **9**, 361; **12**, 655; Phil. Mag. [4] **17**, 301; **27**, 469; also Phil. Trans. (Lond.) (1863), 153, 407; Q. J. Chem. Soc. **17**, 266.

[3] Compt. rend. **100**, 57, 172.

sulphates, phosphates, and any iron and aluminium present; the solution was then filtered and the barium exactly precipitated by dilute sulphuric acid, and then a small quantity of phosphoric acid was added. After the precipitate had settled, the solution was again filtered and subjected to distillation under reduced pressure. The following apparatus was used for this purpose : a large distilling-flask (about 1 l.), with a contraction in the neck near the bulb for the purpose of filling the neck with glass beads; the flask was closed with a two-hole rubber stopper, through one hole of which a thermometer was passed, and through the other a long piece of small capillary tubing, the lower end of which reached to within a few centimeters of the bottom of the flask. This tube was closed at its upper end by means of a piece of rubber tubing provided with a Hofmann screw clamp ; this was for the purpose of regulating the current of air which was passed through the solution, thus preventing the violent bumping which ensues if this precaution be not taken. The distilling-flask was connected by air-tight joints with a condenser and receiver. The exhaustion was produced by means of a powerful water-pump, and the pressure was reduced to 2.5–3 centimeters of mercury. After one-third of the liquid had been distilled off, the distillate was found to contain very little hydrogen peroxide, but a small quantity of hydrochloric acid; another third contained more of the hydrogen peroxide, but still a comparatively small quantity. The beads were then removed from the neck of the flask, and the distillation continued until decomposition began. A small quantity of water was then added and the distillation continued until only a small quantity of liquid remained. The third distillate was found to consist entirely of a moderately concentrated solution of pure hydrogen peroxide, which was further concentrated by freezing out the water and pouring off the liquid remaining. A considerable quantity of this solution, evaporated to dryness, left only the faintest trace of a residue, and tests made showed the entire absence of any of the impurities previously found to be present. The solution itself was found, by using very delicate litmus paper, to be very slightly acid ; this is in accord with the statement made by Hanriot. This solution undergoes no decomposition if kept cold.

For the purpose of determining the molecular weight of hydrogen peroxide, use was made of the apparatus and thermometer

devised and described by Beckmann[1] for the determination of freezing-points of solutions. A glass stirrer was used, and bits of broken glass with sharp edges were put into the apparatus to furnish a starting-point for the formation of ice. Platinum, as is well known, cannot be used, since it acts catalytically, inducing decomposition of the hydrogen peroxide.

Method of Work.—After determining the weight of the empty tube, pure distilled water was introduced by means of a pipette, and the freezing-point noted, several successive determinations being made to insure constancy in the readings. The solution of hydrogen peroxide was then introduced by means of a pipette, the total weight determined to centigrams, and the freezing-point again taken, thus giving the depression due to the hydrogen peroxide (successive determinations made with the same solution showed no change in the readings). The solution was then poured into a beaker, the apparatus washed by successive additions of pure water, the contents of the beaker largely diluted with water, acidulated with sulphuric acid, and the amount of hydrogen peroxide determined by titrating with a very dilute solution of potassium permanganate of known strength. The weight of hydrogen peroxide found subtracted from the total weight of the solution gives the weight of the solvent. The concentration could be changed at will by pipetting into the apparatus water and hydrogen peroxide solution in varying amounts.

The results obtained were in each case satisfactory, the deviations from the calculated values being such as from the nature of the experiment one would expect. The tabulated results follow:

Hydrogen Peroxide, $H_2O_2 = 34$.

Solvent, WATER; molecular depression, 19; depression-coefficient, 0.558.[2]

Wt. Solv.	Wt. Sub.	Concent.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
16.48	0.0207	0.1256	0.069	0.549	18.7	34.6
18.84	0.0509	0.2705	0.151	0.558	19.0	34.0
20.84	0.0761	0.3653	0.216	0 591	20.1	32.1
21.90	0.0943	0.4306	0.246	0.571	19.4	33.3
23.61	0.1211	0.5130	0.288	0.561	19.1	33.9

[1] Ztschr. phys. Chem. **2**, 638.

[2] The results given in this table are exactly as they were found. No determination has been omitted.

Wt. Solv.	Wt. Sub.	Concent.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
37.30	0.2279	0.6110	0.354	0.579	19.7	32.8
29.78	0.1949	0.6544	0.380	0.580	19.7	32.7
19.93	0.1451	0.7280	0.434	0.596	20.3	31.8
17.79	0.1834	1.0310	0.571	0.554	18.8	34.3
19.86	0.2735	1.3773	0.746	0.541	18.4	35.0
17.84	0.2634	1.4767	0.805	0.545	18.5	34.8

For the sake of comparison the tabulated results obtained by Carrara and by Tammann are here given:

Carrara:—*Molecular Weight of Hydrogen Peroxide.*

Concentration.	Depression.	Dep.-coef.	Molec. Dep.	Mol. Wt. found.[1]
0.199	0.120	0.603	20.5	31.5
0.337	0.200	0.593	20.2	32.0
0.382	0.235	0.615	20.9	30.9
0.452	0.265	0.586	19.9	32.4
0.659	0.390	0.591	20.1	32.1
0.662	0.400	0.604	20.5	31.5
0.876	0.500	0.570	19.4	33.3
1.139	0.650	0.570	19.4	33.3
1.554	0.905	0.582	19.8	32.6
2.338	1.350	0.577	19.6	32.9
3.240	1.840	0.567	19.3	33.4
3.295	1.880	0.570	19.4	33.3

Tammann:—*Molecular Weight of Hydrogen Peroxide.*

Concentration.	Depression.	Dep.-coef.	Molec. Dep.[1]	Mol. Wt. found.[2]
0.295	0.109	0.369	12.6	51.4
0.367	0.152	0.414	14.1	45.8
0.457	0.200	0.437	14.9	43.4
0.568	0.279	0.491	16.7	38.6
0.705	0.367	0.520	17.7	36.4
0.873	0.472	0.541	18.4	35.1
1.080	0.609	0.563	19.1	33.6
1.331	0.785	0.589	20.0	32.2

Several points of interest are brought out by a comparison of these tables. First, it will be seen that there is a striking similarity

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[1] Calculated by the authors from the data given by Carrara.

[2] Calculated by the authors from the data given by Tammann.

between the results obtained by Carrara and those obtained inde-
pendently by us, the deviation from the calculated values for
the molecular depression and for the depression-coefficient being
slight in both cases, and not more than can be explained by the
deviations ordinarily to be expected in such determinations. These
deviations are somewhat less in our results than in those of Car-
rara, which may be explained upon the assumption that the solu-
tion of hydrogen peroxide used by us was purer than that used by
him ; or possibly it may be owing to slight errors in his determin-
ations of the freezing-points, since he does not seem to have read
the thermometer usually beyond the hundredths of a degree,
whereas it is possible to obtain readings correct to within one
thousandth of a degree by means of a good lens.

It is impossible to reconcile the results obtained by Tammann
with those obtained by Carrara and by us. They are, as Carrara
also points out, exceedingly peculiar, in that with increasing dilu-
tion there is a corresponding decrease in the depression-coefficient
and an increase in the molecular weight found, whereas the
opposite has almost invariably been found to be the case.[1] It is
interesting to note what values for the molecular weight would,
upon this supposition, have been obtained had the dilution been
carried still further.

It seems to us that the only explanation which can be offered
for this peculiar behavior of Tammann's solutions is that, assuming
he had a pure solution of hydrogen peroxide, he used a platinum
stirrer and probably platinum clippings, such as are commonly
used in the apparatus to facilitate the formation of ice. The plati-
num, acting catalytically upon the hydrogen peroxide, would
cause decomposition, and such decomposition would naturally pro-
duce in the final results a greater proportionate error the more
dilute the solution. His use of interpolation-formulas in a case
where there is such a wide difference in the results obtained is
scarcely justifiable.

THE MOLECULAR WEIGHT OF BENZOYL PEROXIDE.

Of the various derivatives of hydrogen peroxide which have
been described, we selected benzoyl peroxide as the one best
suited for our purpose, because of the ease with which it is pre-
pared in pure condition and because of its comparative stability.

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[1] *Cf.* Beckmann's results, Ztschr. phys. Chem. **2**, 715; **7**, 323.

Preparation of Benzoyl Peroxide.—Benzoyl peroxide was pre-pared by the method given by Brodie. Benzoyl chloride, free from phosphorus oxychloride, was mixed in a vessel with a small quantity of water,[1] a little less[2] than the equivalent amount of pure barium peroxide hydrate, $BaO_2.8H_2O$, was added, and the whole stirred to a thin paste; action began within a few minutes, accom-panied by a slight elevation of temperature, and was completed in the course of eight to ten hours. The benzoyl peroxide, mixed with some benzoic acid and barium chloride, was obtained as a solid hard mass. This was pulverized, washed with water until free from barium chloride, then treated with a dilute solution of sodium carbonate to remove the benzoic acid, and again washed with water until it no longer had an alkaline reaction. The white, powdered benzoyl peroxide was dried over sulphuric acid in a vacuum and the dried substance recrystallized from boiling ether. After two or three crystallizations the substance was obtained in pure state, in beautiful transparent orthorhombic crystals[3] with a melting-point of 103° C. (uncor.). Brodie gives the melting-point as 103.5° C.

The molecular weight of benzoyl peroxide was determined by the freezing-point, as well as by the boiling-point, method described by Beckmann.[4] Two solvents were used in each case, benzene and glacial acetic acid for the freezing-point determina-tions, and ether and chloroform for the boiling-point determina-tions. Benzene was found to be the best solvent for the freezing-point determinations, since benzoyl peroxide is not very soluble in glacial acetic acid. In working with glacial acetic acid some difficulty was experienced, at first, owing to the absorption of moisture by the solvent during the experiment. This was obviated by passing the platinum stirrer through a small glass tube, fitted tightly into the cork, alongside of the thermometer. The upper end of this glass tube was connected with the stirrer by a small, thin rubber bag. This allowed free play of the stirrer up and down through the tube, but excluded both air and moisture.

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[1] Monatsh. Chem. **7**, 522; Lippmann and Sonnenschein found that the yield was increased by the use of a little water.

[2] It is best to have a slight excess of benzoyl chloride, as barium peroxide decomposes benzoyl peroxide.

[3] An examination of these crystals kindly made for us by Mr. A. S. Eakle of the Geological Department of this University showed the faces ∞ P $\overline{\infty}$, ∞ P $\overline{\infty}$, P $\overline{\infty}$, ∞ P, 3 P, P$\overline{\infty}$. *Cf.* Miller: Proc. Roy. Soc. **12**, 394.

[4] Ztschr. phys. Chem. **2**, 638; **7**, 323; **4**, 543; **6**, 437; **8**, 223.

Chloroform was found to be the best solvent for the boiling-point determinations, because, its boiling-point being higher than that of ether, it was easier to regulate the temperature—an important point in the use of this method—and, moreover, benzoyl peroxide is much more soluble in chloroform than in ether. In both methods the weighed substance was introduced into the apparatus by means of the side tube provided for the purpose, in the form of a compressed tablet.

The results of the freezing-point determinations follow :

Benzoyl Peroxide, $(C_6H_5CO)_2O_2 = 242$.
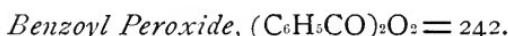
Solvent, BENZENE; molecular depression, 49; depression-coefficient, 0.2023.

Crystallized from acetone—

Wt. Solv.	Wt. Sub.	Concent.	Depres.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
15.62	0.0954	0.6108	0.132	0.2161	52.3	227
	0.2318	1.4840	0.320	0.2156	52.2	227
	0.3998	2.5595	0.544	0.2125	51.4	230
	0.5819	3.7253	0.791	0.2123	51.4	231
	0.7654	4.9000	1.020	0.2084	50.4	235
15.42	0.1472	0.9546	0.199	0.2084	50.4	235
	0.3747	2.4299	0.496	0.2041	49.2	240
	0.5587	3.6230	0.736	0.2031	49.2	241

Crystallized from ether—

15.00	0.1209	0.8060	0.173	0.2146	51.9	228
	0.2483	1.6553	0.348	0.2103	50.9	230
	0.4055	2.7033	0.568	0.2101	50.8	233
	0.5856	3.9040	0.809	0.2072	50.1	236
	0.7933	5.2887	1.089	0.2059	49.8	238
15.00[1]	0.2932	1.9547	0.400	0.2046	49.5	239
	0 6096	4.0640	0.822	0.2023	48.9	242
	0.9810	6.5400	1.311	0.2005	48.5	244

Crystallized from benzene—

13 71	0.1427	1.0408	0.219	0.2104	50.9	233
	0.3320	2.4216	0.503	0.2077	50.2	236
	0.5236	3.8191	0.787	0.2061	49.9	238

[1] This set of determinations was made with a freshly prepared sample of benzoyl peroxide, which was recrystallized from ether four times.

Solvent, ACETIC ACID; molecular depression, 39; depression-coefficient, 0.1611.

Crystallized from ether—

Wt. Solv.	Wt. Sub.	Concent.	Depres.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
16.79	0.1509	0.8982	0.152	0.1692	40.9	230
	0.2954	1.7583	0.294	0.1672	40.4	233
	0.4669	2.7791	0.453	0.1630	39 4	239
19.86[1]	0.2068	1.0413	0.167	0.1604	38.8	243
	0.4218	2.1239	0.331	0.1558	37.7	250
	0.6594	3.3202	0.508	0.1530	37.0	255

The results of the boiling-point determinations are as follows:

Benzoyl Peroxide, $(C_6H_5CO)_2O_2 = 242.$
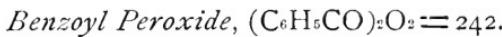
Solvent, ETHER; molecular rise for 100 grams, 21.1°; barometer constant.

Crystallized from ether—

Wt. Solv.	Wt. Sub.	Concent.	Rise.	Mol. Rise.	Mol. Wt. found.
48.79	0.2974	0.6094	0.054	21.3	238
	0.5812	1.1912	0.110	22.3	229
42.50	0.3533	0.8313	0.079	23.0	222
	0.6571	1.5461	0.134	21.0	243
	0.9819	2.3103	0.208	21.8	234
	1.2873	3.0290	0.268	21.4	238
24.72[2]	0.4187	1.6938	0.148	21.2	241
23.94	0.6491	2.7114	0.236	21.1	242
25.34	0.4800	1.8942	0.156	19.9	256
	0.8325	3.2853	0.271	19.9	256

Solvent, CHLOROFORM; molecular rise for 100 grams, 36.6°; bar. 742.5–741.5 mm.

Crystallized from ether—

Wt. Solv.	Wt. Sub.	Concent.	Rise.	Mol. Rise.	Mol. Wt. found.
98.18	0.3945	0.4018	0.063	37.9	233
	0.7573	0.7713	0.120	37.6	235
	1.0459	1.0653	0.160	36.3	244
	1.3295	1.3541	0.196	35.0	253
	1.6303	1.6603	0.234	34.1	260
	1.8820	1.9168	0.270	34.1	260

[1] This set of determinations was made on a freshly prepared sample of benzoyl peroxide which had been recrystallized from ether four times.

[2] These determinations were kindly made for the authors by Mr. B. H. Hite of the Johns Hopkins University.

An attempt was also made to determine the molecular weight of benzoyl peroxide in solution in benzene by the boiling-point method, but it was found that, at the boiling-point of benzene, benzoyl peroxide undergoes partial decomposition.[1] The solution becomes colored and acquires a peculiar odor. Some of the benzoyl peroxide recovered from this solution by allowing the benzene to evaporate spontaneously was found to have a very peculiar odor, and when recrystallized from ether melted at 97°–98°. This low melting-point was probably due to the presence of phenyl benzoate or of diphenyl, products of the decomposition of benzoyl peroxide.

Summary.

1. The results obtained by Carrara, as well as those obtained by us, from the depression of the freezing-point of aqueous solutions of hydrogen peroxide, show that the formula of the substance is H_2O_2, as the molecular weight is not far from 34. This conclusion differs from that deduced by Tammann, but it is probably more correct, being based on more accurate data.

2. The results obtained from the depression of the freezing-point of solutions of benzoyl peroxide show the molecular weight of this substance to be about 242 ; its formula must be, therefore, $(C_6H_5CO)_2O_2$, and consequently that of hydrogen peroxide must be H_2O_2.

3. The results obtained from the rise of the boiling-point of solutions of benzoyl peroxide lead to the same conclusion as that stated in 2., *viz.*, that the molecular weight of benzoyl peroxide is about 242 and its formula $(C_6H_5CO)_2O_2$, and consequently the formula of hydrogen peroxide is H_2O_2.

These results are also in accord with the results obtained by Carrara from determinations of the coefficients of refraction of solutions of hydrogen peroxide.

Cornell University, *April,* 1893.

[1] This is contrary to the statement made by Lippmann that in the cold or at the boiling-point of benzene, benzoyl peroxide undergoes no change.

MIXED DOUBLE HALIDES OF LEAD AND POTASSIUM.

Supplementary Note.

By Charles H. Herty.

While the investigation of mixed double halides of lead and potassium[1] was in progress, the existence of only one bromoplumbite of potassium, $KPbBr_3.H_2O$,[2] was known; consequently, after finding so many of the compounds obtained in that investigation to be mixtures of the simple double salts $KPbI_3.xH_2O$ and $KPb Br_3.xH_2O$, it was deemed unnecessary to make quantitative analyses of the compounds C, D and E in the section "Compounds formed from Solutions containing Decreasing Quantities of Iodine and Increasing Quantities of Bromine." Only qualitative tests were made whereby the presence of iodine and bromine was shown in all of the compounds.

Recently[3] Wells has shown the existence of three other bromoplumbites of potassium, $K_2PbBr_4.H_2O$, $3KPbBr_3.H_2O$, and KPb_2Br_5. It has seemed advisable, therefore, to determine the composition of mixtures in which the bromoplumbite is largely in excess of the iodoplumbite. To this effect the following series of compounds have been prepared and analyzed. Six portions of potassium bromide, 27.35 grams each, were dissolved each in 40.95 grams of water. To one portion was added 3 grams of lead iodide and 4.7781 grams of lead bromide. The mass was then boiled in a flask attached to an inverted condenser until solution was effected. From this solution, on cooling, bundles of lath-shaped crystals separated. These were dried and labeled A. Similarly, to a second portion was added 2 grams of lead iodide and 5.5745 grams of lead bromide. Bundles of lath-shaped crystals were again obtained. These were labeled B. To a third portion was added 1.50 grams of lead iodide and 5.9727 grams of lead bromide. Lath-shaped crystals were again obtained, but the crystal form was very imperfect. These were labeled C. Qualitative tests showed the presence of a large quantity of bromine, but only a slight quantity of iodine, in this compound. To a

[1] This Journal **15**, 81.   [2] *Ibid.* **14**, 124.   [3] Amer. Jour. of Science **45**, 121.

fourth portion was added 0.5 gram of lead iodide and 6.7691 grams of lead bromide. Crystals similar to *C*, but in larger quantity, were obtained. Qualitative tests showed only the slightest trace of iodine. These were labeled *D*. To a fifth portion was added 0.1 gram of lead iodide and 7.0877 grams of lead bromide. Crystals similar to *C* and *D*, but in still larger quantity, were obtained. Qualitative tests showed the presence of bromine alone. These were labeled *E*. Finally, to determine the composition of the salt formed from a solution containing no iodine, there was added to the sixth portion of the potassium bromide solution 7.1676 grams of lead bromide. Crystals similar to *C*, *D* and *E* were obtained in abundance. These were labeled *F*. In the mass of these crystals were noticed several beautiful prismatic crystals, evidently different from the surrounding crystals. These were separated and labeled *G*.

Analyses of Compounds.

1.0011 grams *A* gave 0.0342 gram H_2O; 0.5743 gram $PbSO_4$ = 0.3922 gram Pb; 0.4922 gram K_2PtCl_6 = 0.0793 gram K; 1.1167 grams AgI and AgBr. This last was transformed into 0.8327 gram AgCl, which gives in original substance 0.0688 gram I and 0.4211 gram Br.

1.0012 grams *B* gave 0.0342 gram H_2O; 0.5812 gram $PbSO_4$ = 0.3969 gram Pb; 0.5017 gram K_2PtCl_6 = 0.0808 gram K; 1.1171 grams AgI and AgBr. This last was transformed into 0.8424 gram AgCl, which gives in original substance 0.0358 gram I and 0.4472 gram Br.

1.0016 grams *C* gave 0.0235 gram H_2O; 0.4985 gram $PbSO_4$ = 0.3404 gram Pb; 0.7594 gram K_2PtCl_6 = 0.1223 gram K; 1.1988 grams AgBr = 0.5102 gram Br. The quantity of iodine present in this compound as shown by the qualitative tests is so small that it cannot be accurately determined by conversion of the silver bromide and silver iodide into silver chloride.

1.0010 grams *D* gave 0.0230 gram H_2O; 0.5061 gram $PbSO_4$ = 0.3456 gram Pb; 1.1986 grams AgBr = 0.5101 gram Br; 0.7513 gram K_2PtCl_6 = 0.1210 gram K.

1.0012 grams *E* gave 0.0235 gram H_2O; 0.5068 gram $PbSO_4$ = 0.3461 gram Pb; 1.1983 grams AgBr = 0.5100 gram Br; 0.7503 gram K_2PtCl_6 = 0.1209 gram K.

1.0014 grams *F* gave 0.0217 gram H_2O; 0.5096 gram $PbSO_4$

$= 0.3480$ gram Pb; 1.1963 grams AgBr $= 0.5091$ gram Br; 0.7431 gram $K_2PtCl_6 = 0.1197$ gram K.

0.7202 gram G gave 0.0242 gram H_2O; 0.4255 gram $PbSO_4$ $= 0.2906$ gram Pb; 0.8087 gram AgBr $= 0.3442$ gram Br; 0.3676 gram $K_2PtCl_6 = 0.0592$ gram K.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	3.42	39.18	6.87	42.06	7.92	99.45
B	3.42	39.64	3.58	44.67	8.07	99.38
C	2.35	33.99	Trace	50.94	12.21	99.49
D	2.30	34.53	Trace	50.96	12.09	99.88
E	2.35	34.57	...	50.94	12.08	99.94
F	2.17	34.75	...	50.84	11.95	99.71
G	3.36	40.35	...	47.79	8.22	99.72

Practically all of the water of crystallization was driven off from these salts at 110°. A lost only 0.2 milligram more in weight on raising the temperature of the oven to 200° for two hours, than was lost at 110°; E lost only 1.5 milligrams more.

From the figures in the above table it is seen that so long as the iodoplumbite is present in any appreciable quantity the bromoplumbite is in the form of the salt $KPbBr_3.H_2O$. When, however, only a trace of iodine is present in the compound the bromoplumbite has the formula $K_2PbBr_4.H_2O$, the theoretical composition of this salt being H_2O, 2.89; Pb, 33.21; Br, 51.35; and K, 12.55 per cent.

The salt G, which was found crystallizing in the mass of F, is the salt $KPbBr_3.H_2O$, the theoretical composition of this salt being H_2O, 3.57; Pb, 41.06; Br, 47.61; and K, 7.76 per cent.

The fact that no salt corresponding to the formula $K_2PbBr_4.H_2O$ was obtained in the earlier work upon potassium bromoplumbite[1] is easily explained if the method of preparation used be compared with that used by Wells in the preparation of this salt.[2] It was obtained only when lead bromide was dissolved in very concentrated solutions of potassium bromide. This condition was never met with in my first experiments, for, in them, a solution of lead nitrate was added to a solution of potassium bromide until the precipitated lead bromide no longer dissolved; this precipitation of lead bromide necessarily left a solution much poorer in potassium bromide.

UNIVERSITY OF GEORGIA, *March* 17, 1893.

[1] This Journal **14**, 124. [2] Amer. Jour. of Science **45**, 132.

A MODIFICATION OF THE STANNOUS-CHLORIDE METHOD FOR IRON TITRATIONS.

By R. W. Mahon.

Of the methods which have been proposed for determining iron in its ores, only those depending on titration with permanganate, bichromate, or stannous chloride have come into extensive use. Marguerite's method undoubtedly possesses certain advantages, but the objections to it have caused it to be abandoned by many of those who are engaged daily with iron estimations—among others the writer.

The method proposed so long ago as 1855 by Kessler, and since referred to by him with some minuteness,[1] is an adaptation of the bichromate titration, used extensively, which may be described briefly as follows: reduction of ferric chloride by stannous chloride in excess, and removal of the excess of stannous chloride, after dilution, by mercuric chloride in excess, followed without filtration, by titration with potassium bichromate. This method is accurate and easy of execution. Like all the bichromate titrations, it is, however, dependent upon the testing of drops taken from the solution, with potassium ferricyanide—a tedious operation.

Seeking for a rapid and accurate method of iron-estimation, and one easy of execution, I have observed that ferrous chloride has less affinity for chlorine than mercurous chloride has for chlorine; especially at or near the boiling-heat, and in solutions strongly acid with hydrochloric acid. If, therefore, to a solution of ferric chloride, near the boiling-temperature, containing free hydrochloric acid, and mercuric chloride, a solution of stannous chloride is added, the mercurous chloride, at first formed, redissolves, until all of the iron is reduced to the ferrous condition. A further addition of stannous chloride precipitates mercurous chloride.

In strongly acid solution a considerable excess of stannous chloride is necessary to cause this precipitation. The relation between ferric, mercuric, and stannous chlorides is the same as the relation between ferric, platinic, and stannous chlorides. At or near the boiling-heat, stannous chloride reduces all the iron, in

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[1] Ztschr. anal. Chem. **11**, 249.

solution strongly acid with hydrochloric acid, before reducing platinic chloride. The first drop of stannous chloride in excess reduces platinic to platinous chloride, which is not, however, apparent here, as it remains dissolved in the colorless fluid. If the addition of stannous chloride be continued, the formation of platinous chloride proceeds, and imparts a brownish red color to the solution. If mercuric and platinic chlorides are added to a solution of ferric chloride, strongly acid with hydrochloric acid, at or near the boiling-point, stannous chloride reduces all the iron first, and the first drops in excess cause the formation of a faint cloud of mercurous chloride, darkened and rendered instantly perceptible by finely divided mercury and platinum which are precipitated at the same time. A very minute trace of platinic chloride present in solution is sufficient to bring about this reaction.

This mixture, then, of mercuric and platinic chlorides is an indicator which can be used to advantage in titrations of iron by stannous chloride. In the frequent standardizations of stannous chloride with a standard solution of ferric chloride, which are necessary, it is desirable to employ approximately the same conditions of dilution and acidity, as well as approximately the same quantity of iron, as in the estimations. A correction, as in all titrations dependent on the production of tint imparted to a solution of definite bulk, is to be made. 0.2 cc. of stannous chloride of the strength used imparts a tint to 175 or 200 cc. of solution, which is easily remembered and reproduced. The indicator can be made from a solution of platinic chloride and a solution of mercuric chloride, to contain in one litre, metallic platinum 0.05 gram, and mercuric chloride 34.0 grams. Of such a solution 15 cc. is a suitable quantity to be used in each estimation.

The standard solution of ferric chloride is advantageously made of such strength that 1 cc. contains 0.01 gram of iron; the stannous chloride of approximately the same strength. Some arrangement for preserving the stannous chloride, and introducing it into the burette without unnecessary contact with the air, is necessary, such as that figured on page 409 of the 2d vol. of Fresenius, sixth ed. The burette should be of 100 cc. capacity. A suitable vessel for carrying out the titration is a 600-cc. Erlenmeyer flask.

The estimation of iron in its ores is performed as follows: Weigh accurately about 1 gram of ore into a 250-cc. beaker.

Cover with a watch-glass and digest in 20 cc. of hydrochloric acid, of 1.20 sp. gr., until decomposed. Add now 0.3 gram of potassium chlorate and digest a few moments longer. The glass and the rim of the beaker being washed down into the solution, which should now be about 40 cc. in volume, it is filtered and washed into an Erlenmeyer flask ; 20 to 30 cc. of hydrochloric acid of 1.20 sp. gr., and 15 cc. of the indicator-solution are added. It is now ready for titration. Heat the covered solution to boiling. The trace of chlorine remaining escapes. Lower the light, and titrate at incipient boiling. The residue is prepared for titration by fusing with sodium carbonate, extracting with water and acid, and adding 15 cc. of the indicator. The iron in six ores was determined by the bichromate method (Kessler's), and by the stannous-chloride method with the indicator, with the following results:

$K_2Cr_2O_7$.	$SnCl_2$.
58.67	58.71
39.76	39.61
49.45	49.41
62.49	62.33
55.22	55.11
59.18	59.29

In one ore the iron was determined by three methods, with these results:

$KMnO_4$.	$K_2Cr_2O_7$.	$SnCl_2$.
57.30	57.26	57.33

I have made a large number of titrations by this method, to determine the best conditions of volume, acidity, temperature, and quantities of mercury and platinum to be used, and find them to be as above described.

To recapitulate: the volume of the solution before adding the stannous chloride being about 125 cc., should contain 20 to 40 cc. of hydrochloric acid, sp. gr. 1.20. This should be titrated at or just below incipient boiling, in the presence of a considerable quantity of mercuric chloride and only a trace of platinic chloride.

REVIEWS AND REPORTS.

Recent Progress in Physical Chemistry, III.[1]

Zur Kinetik der in Lösung befindlichen Körper. Nernst: Ztschr. phys. Chem. **2**, 613 (1888).—The amount of a dissolved non-electrolyte S passing through the volume-element qdx of a cylinder will be directly proportional to the cross-section q of the cylinder, to the difference of osmotic pressure dp, and to the time t; but inversely to the distance dx passed through, or $S = -\dfrac{qt}{K} \cdot \dfrac{dp}{dx}$; (1), where the proportionality-factor K denotes the force necessary to give one gram-molecule the velocity of one cm. per second; the *minus* sign is due to the fact that the substance diffuses from a place of greater to one of less concentration. If $c =$ concentration and $p_0 =$ osmotic pressure in a solution having the concentration 1, then $p = p_0 c$ and (1) becomes $S = -\dfrac{qtp_0}{K} \cdot \dfrac{dc}{dx}$; (2). The author calculated the values of K for various substances from the velocities of diffusion, on the assumption that the formula $pv = RT$ holds good for all pressures.

	Urea.	Chloral Hydrate.	Mannite.	Cane Sugar.
T	280.5	282	283	282
$K.10^{-9}$ kg.	2.5	3.8	5.5	6.7

For completely dissociated, binary electrolytes equation (2) will apply if we add a term due to the fact that the two ions must diffuse equally fast in order to prevent an accumulation of free electricity in the liquid. If J_K and J_a be the value of K for the cation and the anion respectively, and u and v the migrating velocities of the same, the correction for the cation will be $\dfrac{p_0}{J_K} \cdot \dfrac{u - v}{u + v} \cdot \dfrac{dc}{dx}$, and for the anion, $\dfrac{p_0}{J_a} \cdot \dfrac{u - v}{u + v} \cdot \dfrac{dc}{dx}$, whence

$$\left. \begin{array}{l} S_K = -\dfrac{qtp_0}{J_K}\left(1 - \dfrac{u - v}{u + v}\right)\dfrac{dc}{dx} = -\dfrac{qtp_0}{J_K} \cdot \dfrac{2v}{u + v} \cdot \dfrac{dc}{dx} \\[2mm] S_a = -\dfrac{qtp_0}{J_a}\left(1 - \dfrac{v - u}{u + v}\right)\dfrac{dc}{dx} = -\dfrac{qtp_0}{J_a} \cdot \dfrac{2u}{u + v} \cdot \dfrac{dc}{dx} \end{array} \right\} \quad (3)$$

Equation (3) can be used to determine S_K and S_a when J_K, J_a, u and v are known. The theoretical results vary from the observed data in few cases by more than 10 per cent.

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[1] The present report outlines the main features of the recent work of Nernst, whose papers on Chemical Theory have, for brilliancy and importance, already become classics. Two of them: Ztschr. phys. Chem. **4**, 372 and **9**, 137, have been included in the previous reports.— J. E. T.

When the dissolved substance is a partially dissociated electrolyte we can consider the undissociated salt as diffusing also, and have a combination of equations (2) and (3). The case of the mixture of two salts having a common ion is similar in principle to that of a single salt, except that we have here the condition that the amount of the common ion passing through the volume-element must be equal to the sum of the amounts of the two other ions passing through the same volume in the same time. Although the general idea of this case is simple, the mathematical statement of it presents such difficulties that the author contented himself with approximations, the details of which, together with the paragraph on the change of the coefficient of diffusion with the temperature, cannot be given here. W. D. B.

Die elektromotorische Wirksamkeit der Ionen. Nernst: *Ztschr. phys. Chem.* **4**, 129 (1889).—If the migrating velocities of the cation and anion be u and v respectively, the work done in carrying the cation from a place of osmotic pressure p_1 to one of p_2 will be $\frac{u}{u+v}\int_{p_1}^{p_2} Vdp$, and to bring the anion from p_2 to p_1, $\frac{v}{u+v}\int_{p_2}^{p_1} Vdp$. Substituting for V from Boyle's Law $pV = p_0$ and integrating, we have for the work, or the electromotive force, the expression

$$E = \frac{u-v}{u+v} \cdot p_0 \log \frac{p_1}{p_2}. \qquad (1)$$

If $u > v$ and $p_1 > p_2$, E is positive and the current flows through the cell from the more to the less concentrated solution. The value of the E. M. F. is seen to depend, not on the absolute values of p_1 and p_2, but on their ratio. Substituting for p_0 we have

$$E = \frac{0.860\, T\,(u-v)}{u+v} \cdot \log \frac{p_1}{p_2} \times 10^{-4} \text{ volts.} \qquad (2)$$

In the following cell p_1 and p_2 denote the osmotic pressures of the ions in the different solutions, u_1, u_2, and v_1, v_2 the migrating velocities of the cations and anions respectively,

$$\text{El.}\, p_1 u_1 v_1 \overset{1}{\mid}\, p_2 u_1 v_1 \overset{2}{\mid}\, p_2 u_2 v_2 \overset{3}{\mid}\, p_1 u_2 v_2 \overset{4}{\mid}\, p_1 u_1 v_1 \text{El.}$$
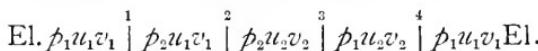
The circuit is closed by like electrodes in the same solution p_1, u_1, v_1; so that no E. M. F. is generated at these contacts. The E. M. F.'s at contacts 2 and 4 are equal and opposite, and we have only to consider those at 1 and 3, which by (2) will be

$$E = 0.860\, T \left[\frac{u_1 - v_1}{u_1 + v_1} - \frac{u_2 - v_2}{u_2 + v_2} \right] \log \frac{p_1}{p_2} \times 10^{-4} \text{ volts.} \qquad (3)$$

If $\frac{u_1 - v_1}{u_1 + v_1} > \frac{u_2 - v_2}{u_2 + v_2}$ and $p_1 > p_2$ the current will flow through the cell from the more to the less concentrated solution. This was

confirmed in every case. The calculated E. M. F. was 13 per cent. higher than the observed when salt solutions were used, 6 per cent. for acid solutions. The reason for this variation is not yet known.

If we have an electrode, non-polarizable in regard to the cation —such as a metal in a solution of its own salt—the work necessary to force the amount of the cation bearing the unit quantity of electricity, out of the solution, will be, if p is the osmotic pressure of a univalent cation,

$$dE = -Vdp = -p_0 d \log p, \quad E = -p_0 \log p + p_0 \log P = p_0 \log \frac{P}{p},$$

where $p_0 \log P$ is the constant of integration. Substituting for p_0,

$$E = 0.860 \, T \log \frac{P}{p} \times 10^{-4} \text{ volts.} \tag{4}$$

For an electrode, reversible in regard to the anion, such as silver, silver chloride in a chloride solution, we have

$$E = 0.860 \, T \log \frac{p}{P'} \times 10^{-4} \text{ volts.} \tag{5}$$

These formulæ were not tested directly, but were developed in order to make the E. M. F. of another form of concentration-cell capable of calculation. For a cell of the type Ag, p_1 AgNO$_3$ | p_2 AgNO$_3$, Ag, we have from (2) and (4),

$$E = 0.860 \, T \left[\log \frac{P}{p_1} + \frac{u-v}{u+v} \cdot \log \frac{p_1}{p_2} - \log \frac{P}{p_2} \right] \times 10^{-4} \text{ volts,}$$

$$E = 0.860 \, T \cdot \frac{2v}{u+v} \cdot \log \frac{p_2}{p_1} \times 10^{-4} \text{ volts.} \tag{6}$$

The corresponding formula for a cell non-polarizable in regard to the anion is

$$E = 0.860 \, T \cdot \frac{2u}{u+v} \cdot \log \frac{p_1}{p_2} \times 10^{-4} \text{ volts.} \tag{7}$$

Equation (7) was tested by the author in a large number of cases and the agreement between theory and experiment was very satisfactory.

The author showed further that the (apparently) very different formula of Helmholtz, connecting the E. M. F. of concentration-cells with the vapor-pressures of the solutions, reduces to formula (6) when one substitutes van't Hoff's expression for the change of the vapor-pressure with the concentration.

The term P in formulæ (6) and (7) expresses the tendency of the electrode to go into solution, thus corresponding to the vapor-tension of a liquid. As we must admit the existence of a vapor-tension, though a very small one, for metals, they must have a solution-tension also.[1] The reason given by Helmholtz and

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[1] Or Vapor-pressure and Solution-pressure, the terminology adopted elsewhere in these reports.—J. E. T.

Nernst why the metals do not dissolve more is that the metal goes into solution as an ion and, with the enormous electrical charges which the ions are assumed to have, equilibrium takes place before an appreciable quantity has been dissolved. This view offers no explanation for the fact that metallic vapors do not conduct.

The author obtained an expression for the E. M. F. of a concentration-cell where the solutions are at different temperatures, by substituting for p from the van't Hoff expression $p = a\mu T$, where $a =$ constant and $\mu =$ concentration in gram-equivalents per liter. In cells with mercury electrodes the current passed through the solutions from the cold to the warm contact. The numerical results obtained between different ranges of temperature were thoroughly discordant.

In closing, the author treated the effects upon the electromotive forces of several of the non-polarizable cells in actual use, due to the changes of concentration in the component solutions. His qualitative conclusions were in all cases in accordance with the facts; quantitative predictions were impossible, the solution tensions of the metals being not yet determined.

This paper is one of the most important in modern physical chemistry and deserves careful study, both for the ideas developed in it and on account of the vast amount of important research which it not only suggests but makes necessary. w. d. b.

Ueber ein neues Prinzip der Molekulargewichtsbestimmung. W. *Nernst: Ztschr. phys. Chem.* **6**, 16 (1890).—Dissolved substances decrease the vapor-pressures of their solvents;[1] they must also decrease in the same manner the solution-pressures[2] of these solvents as towards a second liquid. In order to derive strictly the relation between solubility and osmotic pressure the author presupposes the equation of condition of dissolved substances, $pv = RT$, and the expression for the work required to compress a dissolved gram-molecule from the volume v_1 to v_2, *i. e.*,

$$\int_{v_2}^{v_1} p\,dv = RT \int_{v_2}^{v_1} \frac{dv}{v} = RT \log \frac{v_1}{v_2} = RT \log \frac{p_2}{p_1}.$$

Suppose in contact two liquids, A and B, very slightly reciprocally soluble, N gram-molecules of A containing in solution n gram-molecules of a substance of osmotic pressure π; suppose also pure solvent A in contact with B. This gives two pairs of liquids: (I) solution in A; (Ia) solution of A, with osmotic pressure p', in B (in equilibrium with I); (II) pure A; (IIa) saturated solution of A, with osmotic pressure p, in B.

Carry a gram-molecule of A in isothermal, reversible cycle from I to Ia where it fills volume v' (work done, $-p'v' = -RT$); from Ia to IIa (work done, $+ RT \log \dfrac{p}{p'}$); from IIa to II (work done,

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[1] *Cf.* This Journal **15,** 138.　　　　[2] *Ibid.* **15,** 141.

$pv = + RT$); from II to I, S = molecular volume of A, (work done, $- \pi S$). Here Σ work $= 0$ (2d Law of Thermodynamics), so $\pi S = RT \log \frac{p}{p'}$. Substituting for $\log \frac{p}{p'}$ A's relative solubility-depression $\frac{p-p'}{p}$ and for π and $\frac{V}{S}$ their values $\frac{RT}{V}$ and $\frac{N}{n}$ (V is volume of I per gram-molecule dissolved substance), we have $\frac{p-p'}{p} = \frac{n}{N}$. This is also the equation for van't Hoff's vapor-pressure law of solutions.[1] In words: on adding a foreign substance to a solvent, the relative solubility-depression of the latter towards a second liquid is the ratio of the number of molecules added to the number of those of the solvent.

Dissolving in 100 grams valeric acid g grams of a substance of molecular weight M, $n = \frac{g}{m}$ and $N = \frac{100}{102}$, hence $M = \frac{102g}{100} \cdot \frac{p'}{p-p'}$. The solubility p of valeric acid in water was found by titration, the decrease $p - p'$ by a subsequent titration, after adding to the excess of acid the substance to be studied. The molecular weights thus found by a single titration were, *e. g.*,

	Mol. wt.	Found.
Chloroform	119.5	118
Menthol	156	161
Stearic acid	284	291

Excellent results were obtained also from the depression of the solution-pressures of ether and of ethyl acetate towards water.

Additional data and specific instructions for a practical method for accurate work are given in a later paper.[2] 20 cc. ether (freed from alcohol by shaking out with water and drying over sodium) and 5 cc. water are placed in a Beckmann freezing-apparatus. Add the substance (which must be quite insoluble in water), g grams per 100 grams ether; from the total ether used subtract 0.8 gram, the amount dissolved by the water. The freezing-point rises $t°$ from about $-3.85°$. The corrected rise of freezing-point is $t' = t \cdot \left(1 + \frac{t}{3.85}\right)$, the molecular weight is $M = E \cdot \frac{g}{t'}$. The "molecular rise" E is 3.06. With vigorous super-cooling very accurate readings are obtainable. Results cited are, *e. g.*,

	Mol. wt.	Found.
Benzene	78	78–82
Naphthalene	128	128–131
Carbon bisulphide	76	72–78

Ein osmotischer Versuch. W. Nernst: *Ztschr. phys. Chem.* 6, 37 (1890).—That the singular action of semi-permeable mem-

[1] *Cf.* This Journal **15**, 138.   [2] Ztschr. phys. Chem. **6**, 573.

branes is accounted for by the solubility law derived in the preceding paper is illustrated by the following experiment: Over an inverted funnel-tube is stretched a porous membrane saturated with water, the funnel containing a solution of benzene in ether, and being submerged in ether.   The solution and the pure ether are thus separated by a water-layer, towards which the solution-pressure of the first is diminished by the presence of the benzene, which, being insoluble in water, cannot of itself pass the membrane.   The excess of pressure of the pure ether towards the water layer causes it to diffuse through the membrane, diluting the benzene solution and raising its level in the tube until the pressure-difference is counterbalanced by the weight of the column.   The ether used is first saturated with water to prevent it dissolving the water-layer.   According to this, the activity brought about by the osmotic pressure in plant-cells is due to the solubility of water, and the non-solubility of the dissolved substances of the sap, in protoplasm.

Verteilung eines Stoffes zwischen zwei Lösungsmittel und zwischen Lösungsmittel und Dampfraum. W. Nernst: Ztschr. phys. Chem. **8**, 110 (1891).—In this very important paper Nernst has developed the theory of the vapor-pressures of solutions of volatile substances, and that of the distribution of a dissolved substance between two solvents.   From van't Hoff's law, that a substance having the same molecular weight in gas and solution dissolves proportionally to its gas-pressure, he arrives at the Law of Distribution :—*At a given temperature each sort of molecule has a constant ratio of distribution between solvent and vapor, or between two solvents, independent of the presence of other sorts of molecules, and whether reacting chemically with them or not.* Different "sorts of molecules" are not only those of different substances, but also double molecules, single molecules, and different ions.   Comparison with known data on the distribution of bromine or iodine between water and carbon bisulphide (Br_2 and I_2 in both solvents) shows a satisfactory agreement.   Experiments with salicylic and with benzoic acids shaken with water and benzene—these acids being largely bimolecular in benzene and somewhat dissociated into ions in water—show the *total concentrations* in the two solvents not even approximately proportional, the concentrations of the normal molecules, however, to be entirely so.

When N gram-molecules solvent contain n gram-molecules of a volatile substance whose molecular weight is the same in solution and in vapor, the composition of the vapor of the solution is readily found.   Here the partial pressure p of the dissolved substance is proportional to its concentration $\frac{n}{N+n} = kp$, that of the solvent is $P = P_0 \frac{N}{N+n}$, P_0 being its vapor-pressure in pure con-

dition. The molecular concentrations in the vapor are then, of course, given by these values of p and P. The formulæ represent more closely the measurements of Winkelman than does the similar theory of Planck.[1]

The most interesting case is that of a substance having different molecular condition in solution and gas, as acetic acid, which is almost entirely bimolecular in benzene but largely monomolecular as vapor. Setting proportional the concentrations of the normal molecules in both solution and vapor, an expression for p is obtained, which yields results in striking agreement with the values found directly from the boiling-points of the solutions. With barometric pressure $B = 750$, $p = B - P$ and, combining with van't Hoff's vapor-pressure formula, $p = B - P_0 \dfrac{N}{N+n}$, n dissolved molecules causing $\lrcorner T$ change of boiling-point, P_0 at the actual boiling-temperature becomes $P_0 = B + \dfrac{dP_0}{dT} \cdot \lrcorner T$, and so $p = B\left(\dfrac{n}{N+n} - \dfrac{dP_0}{dT} \cdot \dfrac{\lrcorner T}{B} \cdot \dfrac{N}{N+n}\right)$. $\dfrac{dP_0}{dT} = 22.2$ is found from $\dfrac{dP_0}{dT} = \dfrac{o}{Tv}$ (Clausius), and the gas-equation. Terming C the actual total molecular concentration $\dfrac{n}{N+n}$, the dissociation being found from the freezing-points, the desired pressure is

$$p = 750\,C - 22.2\,\lrcorner T(1 - C) \text{ mm. mercury.} \tag{1}$$

From the dissociation-isotherm $\dfrac{m\alpha}{1-\alpha} = k$ (m and $\alpha =$ percentage concentration and dissociation, respectively), the concentration of the normal molecules in the solution is proportional to $\sqrt{m(1-\alpha)}$. From the density, $\lrcorner$, of the vapor, and its theoretical density, δ, at dissociation $\alpha' = 0$, results $\alpha' = \dfrac{\delta - \lrcorner}{\lrcorner}$, and the concentration of the normal molecules in the vapor is $p\lrcorner \cdot \dfrac{\delta - \lrcorner}{\lrcorner} = p(\delta - \lrcorner)$. The Law of Distribution requires $14.4\sqrt{m(1-\alpha)} = p(\delta - \lrcorner)$, or

$$p = 14.4 \dfrac{\sqrt{m(1-\alpha)}}{\delta - \lrcorner} \text{ mm. mercury,} \tag{2}$$

the proportionality-factor, the inverse solubility-coefficient of the normal molecules, being 14.4. A few of the results, giving the partial pressures of the acid-vapor, as directly found from (1), and as found from the Law of Distribution from (2), are:

Grams acid.	α.	p from (1).	p from (2).	Δ.	α'.
0.663	0.10	6.6	6.5	2.44	0.70
5.00	0.038	23.6	23.9	2.83	0.47
8.42	0.029	36.4	36.5	3.02	0.36

[1] Ztschr. phys. Chem. **2**, 405.

This agreement is one of the most brilliant achievements of the modern Physical Chemistry. Similar experiments with solutions of water in ether led to the result that, of the $(H_2O)_2$ molecules present in a 1.315-per cent. solution, about 58 per cent. are dissociated into the simple molecules H_2O. In connection herewith Walker's conclusion, that water in ether is *almost entirely* bimolecular,[1] is shown to be incorrect, his formulæ requiring the solubility of pure water, not of water saturated with ether, in ether.

Qualitative application of the theory shows that, for example, the partial pressure of hydrochloric acid over its aqueous solution increases, if an electrolyte with a common ion be added; decreases, if the second electrolyte have not a common ion; that in concentrated solution salicylic acid will be in great measure taken up by benzene, if dilute will go into the water-layer, but can be driven into the benzene by adding a strong acid or a salicylate. Further applications suggest themselves.

Ueber die Maximaltension, mit welcher Wasserstoff aus Lösungen durch Metalle in Freiheit gesetzt wird. G. Tammann und W. Nernst: Ztschr. phys. Chem. **9**, 1 (1892).—A metal acting upon aqueous acids liberates hydrogen, whose partial pressure when in equilibrium with metal and solution is termed its "maximum pressure" p. The work gained in liberating 2 grams hydrogen, transferred to pressure P, is $W = pv + RT \log \dfrac{p}{P}$. The work gained in a Daniell's cell in dissolving 1 gram-molecule of zinc and precipitating 1 gram-molecule of copper is then $W_1 - W_2 = RT \log \dfrac{p_1}{p_2}$, which is equal to the E. M. F. E; or

$$E = 0.430\, T \times 10^{-4} \log \frac{p_1}{p_2} \text{ volts.}$$

This relation renders possible for the first time a calculation of the E. M. F. of a reversible element from accessible, extraneous data. Combination with the Clausius vaporization-formula yields the famous equation of Helmholtz, $W - E = -T \cdot \dfrac{dE}{dT}$.

According to Nernst's electrolytic solution-pressure theory, a metal drives another out of solution by reason of its superior solution-pressure, and a metal liberates hydrogen with acids only when the pressure of the gas over its solid solution in the metal exceeds one atmosphere.

In the experimental work of the authors, metal and acid were brought together in sealed tubes, the pressure of the freed hydrogen being measured manometrically. Their apparatus usually exploded at pressures approximating 70–90 atmospheres, proving the electrolytic solution-pressures of the metals to be great.

[1] *Cf.* This Journal **15**, 143.

Successful experiments with dilute acids showed the pressure rapidly to increase with the acid-concentration and to be strongly depressed by the presence of neutral salt.

Osmotischer Druck in Gemischen zweier Lösungsmittel. W. *Nernst: Ztschr. phys. Chem.* **11**, 1 (1893)—If a mixture of solvents contain in volume v 1 gram-molecule of dissolved substance of osmotic pressure π, removal of v therefrom requires work πv. This can be accomplished by isothermal vaporization. Suppose v composed of n_1 and n_2 gram-molecules of each component, respectively: their partial pressures over pure mixture and solution being p_1, p_1' and p_2, p_2' respectively. Transferring the n_1 gram-molecules from solution to pure mixture requires work $n_1 R T \log \frac{p_1}{p_1'}$; transferring both n_1 and n_2 requires then

$$\pi v = n_1 R T \log \frac{p_1}{p_1'} + n_2 R T \log \frac{p_2}{p_2'} = R T; \text{ or } n_1 \log \frac{p_1}{p_1'} + n_2 \log \frac{p_2}{p_2'} = 1.$$

It is proposed to determine the pressures entering into this equation, from the boiling-point changes of the solutions and the composition of their vapors. Accounting for the variation of pressure with temperature, by application of the Clausius vaporization-formula $\frac{dp}{dT} = \frac{\rho}{Tv}$, and making the necessary reductions, there results

$$\frac{1}{E} = \frac{1}{E_1} \cdot \frac{q}{100} + \frac{1}{E_2} \cdot \frac{100 - q}{100}.$$

E, E_1 and E_2 represent the molecular rise of boiling-point for the mixture and for each component, the mixture consisting of q grams of one, per 100 grams of both, *i. e.*, the molecular rise of boiling-point is simply additive.

Studien über die Verwendbarkeit des Beckmannschen Siedeapparates. *Max Roloff: Ztschr. phys. Chem.* **11**, 7 (1893).—Careful determinations of the boiling-points of aqueous solutions of potassium chloride are compared with the vapor-pressures of water at the same temperatures, to obtain the relative depressions. The osmotic pressures are calculated therefrom according to the ordinary van't Hoff formula: $\pi = R T \cdot \frac{s}{M} \cdot \log \frac{p_1}{p}$. M is the molecular weight of potassium chloride; s the specific gravity of the solution. Tabulated values from 3.23 to 112.3 atmospheres and the corresponding $\lrcorner T$'s are given.

With the boiling-point method are obtained the individual partial pressures in the vapors of aqueous solutions of formic, acetic, hydrochloric and nitric acids of varying concentrations. The theory is that of Nernst, as reviewed above.

Nernst's theory of the osmotic pressures of solutions in mixed solvents is tested in the manner indicated in the preceding review.

Solutions of naphthalene in benzene and chloroform and of boric acid or potassium chloride in water and acetic acid are studied, and a brilliant agreement with the theory demonstrated.

The Beckmann boiling-point apparatus is adapted to determinations under varying pressures by connection with an air-pump and an oil manometer. The method shows a surprising accuracy and is applied in determining the change of boiling-point of water with the temperature. Figures agreeing with the famous determinations of Regnault are readily obtained. Extensive application is prophesied for the new method.

Ueber die Farbe der Ionen. W. Ostwald : Ztschr. phys. Chem. **9,** 579 (1892).—Experience regarding absorption-phenomena of undissociated compounds in solution shows substitution in the molecule to effect distinct alteration in the light-absorption and color. In a salt-solution of finite concentration, the absorption-spectrum of the electrically neutral molecules present, together with that of each of the ions, constitutes that of the solution. At high dilutions, where the dissociation is quite complete, all salts with the same colored ion must have the same absorption-spectrum and color, if the other ion be colorless. To establish this conclusion, as against the statements of Krüss[1] and Knoblauch,[2] the author both measured and photographed the absorption-spectra of about 300 salts, including, *e. g.*, 17 salts of diazo-resorcin and 20 of para-rosaniline. The published measurements and heliotype prints conclusively show the spectra of dilute solutions of different salts with the same colored ion, to be identical. Ewan has reached the same result for solutions of copper salts.[3]

Ueber Azofarbenspektra. C. Grebe: Ztschr. phys. Chem. **10,** 673 (1892).—References to the recent literature showing changes in the molecule to condition corresponding changes in the absorption-spectrum are given by Vogel[4] and Schütze.[5] Vogel emphasizes the influence of the *position* of the substituents, Schütze the relation between constitution and color. To obtain extended and comparable results Grebe studies the relation between the constitution and absorption-spectra of over one hundred azo-dyestuffs in solution in concentrated sulphuric acid. Curves representing the intensity of the absorption accompany the paper. With increasing number of carbon atoms the absorption-bands moved without exception from violet towards the red. Substituting hydroxyl or the amido group produces the same effect. The opposite effect is produced by the sulpho group, the numerical value of the change being always practically the same. The position of the substituents has an entirely regular influence.

[1] Ztschr. phys. Chem. **2,** 320 (1883).
[2] Ann. der Phys. Wied. **43,** 767 (1891).
[3] Ewan: Phil. Mag. **33,** 317 (1892).
[4] Ann. der Phys. Wied. **43,** 449.
[5] Ztschr. phys. Chem. **9,** 109.

Methyl- und Ethylalkohol als Lösungsmittel. C. A. Lobry de Bruyn: Ztschr. phys. Chem. **10**, 782 (1892).—Determinations of the solubilities of about forty anhydrous substances, mostly salts, at 15°–25°, confirmed the rule of Dumas and Péligot that in solvent power methyl alcohol stands between ethyl alcohol and water. Hydrochloric acid, mercuric chloride and iodide and the aromatic nitro compounds form exceptions. Methyl alcohol replaces the two molecules of water of crystallization in copper chloride, barium bromide, mercuric chloride, and cobalt sulphate; ethyl alcohol, however, does not. The sulphates with water of crystallization dissolve in methyl alcohol to as much as 60 per cent., but these concentrated solutions are mostly unstable, those of zinc, copper, cobalt, and magnesium precipitating crystals in a few minutes, others, as of nickel and iron, after days or weeks. This almost entirely decolorizes the solutions of salts of nickel, copper and cobalt. The salt $NiSO_4.6H_2O$ remains in solution. A few drops of water, or a temperature-rise, greatly accelerates the precipitation in all cases. The solution of the salt $MgSO_4.7H_2O$ clouds on heating, but clears again on cooling. The precipitates are, in some cases, crystals with less water; in others the water is partially replaced by alcohol. Similar phenomena with ethyl alcohol are less striking, since it dissolves the salts to only 1 or 2 per cent. The author suggests that these hydrates may exist as such in solution in methyl alcohol.

Ueber Oxydationsketten. W. D. Bancroft: Ztschr. phys. Chem. **10**, 387 (1892).—By means of a galvanometer the author measured the E. M. F. of systems composed each of an oxidizing and a reducing agent separated by an indifferent salt solution or by mercury. The E. M. F. of the cells was found to be, within the experimental error of about ±0.02 volts, independent of the nature of this connection, as well as of that of the electrodes, which were for the most part of platinum. It was shown further to be additive, being the sum of the potential differences of electrode and solution; extended tables of these experimentally determined differences are given. It was found also to remain constant for a wide range of concentrations. The nature of the indifferent (not oxidizing or reducing) ion exerts no effect upon the E. M. F., except that a free acid is a stronger oxidizing agent than is the corresponding salt, the contrary holding for reducing agents.

TREVOR.

CORNELL UNIVERSITY.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR H. ELLIOTT, Ph. D., Professor of Chemistry and Physics and Director of the Chemical Laboratory in the College of Pharmacy of the City of New York. Published by the Author.

Books for laboratory instruction in qualitative analysis are so numerous that they can vary but little. In Prof. Elliott's book

the list of the commercial compounds of each metal is of value to the student. The special tests for the single metals are well chosen; the directions for separating the metals are very clear and contain many minor details indispensable to the operations, but usually omitted from books of this kind. Herein lies the value of the book, which can be recommended as an excellent manual. While commending the book, one may differ from the author as regards methods of laboratory instruction. To quote from the introduction : "Above all things the student should work with the instructor, and at exactly the same moment, upon the same materials and with a parallel set of apparatus, thus insuring success and giving a confidence inspired by no other method of working. The method here described can be readily applied in classes of one hundred if the instructor is on a raised rostrum where he can be easily seen by every member of the class." If an instructor has to struggle single-handed with a class of a hundred students this method is, doubtless, the best under the circumstances, but then it is the circumstances which are wrong. Surely in the laboratory each student should work independently, neither held back nor dragged on by others. The instructor should study each individual student and demand work from him in proportion to his ability. Where each instructor has not more than fifteen or twenty students to care for on a given day this is possible ; with limited time and unwieldy classes it is not, and then the " test-tube drill " and similar devices for mass-instruction come into play.   E. R.

NOTES.

A New Electric Furnace.

Henri Moissan describes[1] a furnace in which the heat of the electric arc is utilized. The furnace is a chamber of carbon having the form of an upright cylinder, standing on a carbon plate, and covered with a carbon disk. The cylinder is placed in a block of quicklime, an air space of 5 mm. being left between the cylinder and the lime. The dimensions of a furnace for a current of 300 to 500 ampères are 6 cm. in height, 5 cm. in diameter. The horizontal carbon electrodes are 3 cm. in diameter, and pass through circular openings cut in the cylinder and in the block of lime; they are so mounted that the distance between their points can be regulated. The current is furnished by a dynamo.

Moissan says that the only limit to the obtainable temperature is that of the electric arc, and that temperatures above 3000° are readily obtained.   E. R.

[1] Compt. rend. **116**, No. 3.

Studies on the Properties of Carbon, and the Preparation of Diamond.[1]

Henri Moissan describes in No. 7, the analysis of a meteorite found in the Cañon Diablo in Arizona, and presented to the French Academy. One fragment had on its surface a point of great hardness, which scratched steel, and was surrounded by carbon and iron carbide. Moissan treated the fragment by Berthelot's methods, to remove foreign matter and separate from each other different forms of carbon. Berthelot has shown that a mixture of nitric acid and potassium chlorate oxidizes amorphous carbon completely to carbon dioxide, graphites to graphitic acid, or graphitic oxides, and does not attack diamond. The fragment was treated with boiling hydrochloric acid till all iron was dissolved. The residue contained (1) a fine powder of carbon, perhaps resulting from the decomposition of iron carbide; (2) carbon in minute fragments, brown in color, resembling the carbon found in suddenly-cooled cast iron; (3) a carbon of high density in rounded fragments mixed with iron phosphide and metallic nickel. After treatment with boiling sulphuric acid and with hydrofluoric acid alternately (which removed everything excepting carbon), the density of the residue was found greater than that of methylene iodide. It was then treated eight successive times with a mixture of boiling nitric acid and potassium chlorate. There remained two minute yellow diamonds of specific gravity much greater than methylene iodide, scratching ruby, burning in oxygen to carbon dioxide. The largest diamond measured 0.7 by 0.3 mm.

In another fragment of the meteorite, black diamond, the so-called carbonado, was found. This is the first time that diamond has been found in meteorites.

In the same number of the *Comptes Rendus* is another article by Moissan, giving the analyses of the " blue earth " of the South African diamond-fields. This is a serpentine breccia in which the diamonds are found. Analysis shows that this blue earth contains microscopic transparent diamonds, carbonado or black diamond, and crystallized graphite.

In No. 6 Moissan describes the preparation of diamond by the crystallization of carbon at high temperature and high pressure. His method of work is ingenious. The temperature required was easily reached in the electric furnace described above. To obtain a high pressure at high temperatures, he utilized the increase in volume of fused iron passing from the liquid to the solid condition: iron, like water, expands at the moment of taking the solid form. Pure carbon, prepared from sugar, was tightly compressed into a small wrought-iron cylinder closed by a cap screwed on.

200 grams of wrought iron were melted in a carbon crucible in the electric furnace—an operation requiring only a few

[1] Compt. rend. **116**, Nos. 6, 7, 10, 12.

moments—and the cylinder containing the carbon was then plunged into and completely immersed in the molten iron. The crucible was then lifted from the furnace and placed in a vessel of water, causing the quick formation of an outer layer of solid iron ; when this crust had cooled to a dark-red heat, the crucible was taken from the water and allowed to cool in the air.

On treating the metallic mass with boiling hydrochloric acid until all iron was dissolved, there remained three varieties of carbon: graphite, amorphous brown carbon, and carbon of high specific gravity. When this last was treated by Berthelot's method, as described above, there remained minute diamonds, some black and some transparent, but showing all the properties of diamond.

Moissan varied the experiments: In one series, fused iron saturated with carbon at 2000° was cooled in a current of illuminating gas. This experiment yielded microscopic transparent diamonds resembling those found in the blue earth of the diamond-fields. In another series of experiments silver was substituted for iron, as silver has the same property of expansion on passing from the liquid to the solid state. This series of experiments was very interesting. Of course the temperature required was lower than with iron, and no transparent diamonds were obtained, but an abundance of carbonado; specimens of this from different experiments showed different densities—from 2.5, the density of graphite, to 3.5—thus showing an increasing hardness from amorphous carbon, through the soft and hard graphites and colored diamonds of increasing density, to the transparent diamond. The carbonado of density 3.5 scratches ruby.

Moissan concludes by saying that though he made many trials with the fused iron, in only a few experiments has he succeeded in obtaining transparent diamonds, and then only in minute quantities.

In No. 10, Moissan has an article on the analysis of the ash of the impure diamond, which always contains iron and silicon, and, often, lime.

In No. 12 is an article on a variety of graphite which puffs up when heated on platinum foil, after treatment with nitric acid, behaving somewhat like mercuric sulphocyanide when heated. Prof. Luzi first called attention to this phenomenon,[1] and shows that some natural graphites behave thus, while others do not. Luzi calls the first variety graphites ; the second, graphitites.

Moissan finds that when molten cast iron is suddenly cooled with water, ordinary graphite is formed on the surface, and below the surface another variety of graphite giving Luzi's reaction. To obtain this last variety alone it is better to employ platinum instead of iron. He fuses in the electric furnace 200 grams of platinum in a carbon crucible. The platinum melts rapidly and after a few minutes distils from the crucible as a vapor, condensing in drops

[1] Ber. d. chem. Ges. **25,** 214.

of molten metal on the cooler parts of the electrodes. The liquid platinum becomes rapidly saturated with carbon at this high temperature, part forming a carbide of platinum. On cooling the excess of carbon is found in the form of crystals of graphite scattered throughout the mass. This graphite shows Luzi's reaction.

Moissan has examined the products of this reaction. He finds that oxides of nitrogen and a little carbon dioxide are given off; the swelling up of the graphite on heating is caused by the escape of these gases. The formation of these gases may be due to the presence of small quantities of amorphous carbon between the crystal surfaces of the graphite, or perhaps to the decomposition by heat of a little graphitic oxide, formed by nitric acid attacking the softer particles of graphite. E. R.

Notes on the Rapid Preparation of Refractory Metals at High Temperature.[1]

Moissan has used his electric furnace to prepare uranium, manganese, chromium, cobalt and nickel, by reduction of the oxides of the metals in carbon crucibles. The action is similar to that of a blast furnace, inasmuch as the products are not pure metals, but are carbides of the metals. The proportion of carbon varies in the products of different experiments :

		Percentage of Carbon.
Uranium carbide		5—13.5
Manganese	"	6—14.5
Nickel	"	6—13.5
Cobalt	"	7— ...
Chromium	"	8—12

The only products are carbon and the desired metal : there are no impurities present. The yield is very satisfactory : an ingot of uranium carbide weighing 200–220 grams, was made in ten minutes, with the aid of a current of 450 ampères and 60 volts. The carbide of manganese was prepared in five minutes, with a current of 300 ampères and 60 volts. Chromium carbide was prepared in eight minutes, with a current of 350 ampères and 50 volts.

The reductions can also be made with much weaker currents, requiring more time.

Moissan promises soon to publish methods for obtaining perfectly pure uranium, and manganese from the carbides. To prepare pure chromium from chromium carbide, he breaks the mass into small fragments and brings it into a carbon crucible which has been thickly lined with chromium oxide. The mass is covered with chromium oxide and again heated in the electric furnace. The oxide and carbide are fused, the oxide extracting the carbon

[1] Compt. rend. **116**, No. 8.

from the carbide, which is gradually decarbonized until pure chromium, without a trace of carbon, is obtained. This chromium, heated in a current of dry chlorine, is changed quantitatively into volatile chromium chloride without leaving any trace of residue.

<div align="right">E. R.</div>

Commercial Preparation of the Peroxides of the Alkali Metals.

A method for the preparation of the peroxides of the alkali metals has recently been described,[1] which has as its essential features (1) the use of aluminium for the crucibles to contain the alkali to be oxidized, and (2) the employment for the oxidation of a mixture of oxygen and nitrogen in which the proportion of the latter gas is continually lessened as the process is continued. The temperature is maintained at about 300°.

The alkali is placed in small quantities in trays of aluminium, the latter being arranged on wheels to assist in their introduction into and withdrawal from the furnace. The use of aluminium does away with the difficulties hitherto experienced where, trays of other material (as, for example, glass) being employed, a satisfactory product could not be obtained owing to the corrosion of the material of the tray. The aluminium is entirely uninfluenced by contact with the alkali. The trays are run into a closed retort of iron into which a regulated current of air can be made to pass. The air is, of course, completely freed from moisture and carbon dioxide, and, before entering the retort, is mixed with oxygen or nitrogen as may be desired. By the method of employing at first air poor in oxygen and then gradually increasing the proportion of that gas as the area of oxidizing material increases, a slow and uniform action is brought about, and, as a result, a product of practically constant composition.

The process is patented by the (Castner) Aluminium Company, Limited, of London.

<div align="right">W. W. R.</div>

Errata in the Article on Reduction of Nitric Acid by Copper, by Paul C. Freer and Geo. O. Higley.

Page 71, fourth line from the bottom, nitrogen dioxide should read nitric oxide. *Ibid.*, last line, −12° should read 12°.

Page 72, first and second lines, acid represented by the formula $H_2SO_4 + 9H_2O$ should read, sulphuric acid diluted with water, 1:9. *Ibid.*, fourth line, freezing mixture should read cold water.

Page 71, Reference 2 should read [3] **7**, 38.

Page 72, Reference 2 should read **28**, 828.

<div align="center">[1] Monit. Sc. Quesneville [4] **6**, 869.</div>

AMERICAN

CHEMICAL JOURNAL.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

VII.—ON THE REACTION OF ALCOHOLS WITH PARADIAZO-BENZENESULPHONIC ACID.[1]

By W. B. Shober.

This investigation was undertaken at the suggestion of Professor Remsen, and carried on under his guidance, with the object of determining the action of methyl, ethyl and propyl alcohols on paradiazobenzenesulphonic acid, at various pressures.

16 grams of the diazo compound were boiled with about 250 cc. of methyl alcohol (distilled from lime) under a pressure of 760–780 mm. of mercury. At first the alcohol assumed a yellow color, then changed to pink, and finally the liquid became dark red. The decomposition was slow, about two and a half hours being necessary to decompose all of the diazo compound. The liquid obtained in this way is very strongly acid. The alcohol was distilled off, leaving a dark syrupy residue. Repeated attempts to obtain crystals from this residue, after purification with animal charcoal, were unsuccessful. The residue was dissolved in water and boiled with animal charcoal, nearly all the color being removed by this means. It was then neutralized with barium carbonate; a slight precipitate of barium sulphate was formed which was filtered off. The sodium salt, or rather salts (for, as shown below, two reactions took place), were made by precipitating the barium as carbonate. It was found necessary to use

the sodium compound, as the corresponding barium salts do not react readily with phosphorus pentachloride. The sodium salts were treated with one molecule of phosphorus pentachloride. The action takes place easily without the aid of heat. When the reaction was completed the flask containing the products was heated to 120° in a sulphuric-acid bath, in order to drive off the phosphorus oxychloride. The sulphonic chlorides were washed with a large amount of water. Concentrated ammonium hydroxide was then poured over the oil and the mixture allowed to stand for some time. The amides thus obtained were boiled with animal charcoal and recrystallized several times. Two different kinds of crystals were found which were separated by mechanical means. One substance crystallized in beautiful, long, slender needles, the melting-point of which was found to be 113°. This substance is shown by the analysis given below to be methoxy-benzenesulphonamide, presumably the para modification, a compound which I believe has not been described before. The other compound found also crystallizes in needles, but they are much smaller. Its method of formation and melting-point (154°) show it to be parabenzenesulphonamide. The substance melting at 113° is insoluble in cold water, easily soluble in hot water and in alcohol. Analysis shows its composition to be $C_7H_9SNO_3$. The results obtained are as follows:

I. 0.29537 gram of the substance gave 0.36758 gram barium sulphate, corresponding to 17.10 per cent. of sulphur.[1]

II. 0.12373 gram of the substance gave 0.15517 gram of barium sulphate, corresponding to 17.23 per cent. of sulphur.[1] These determinations were made by Liebig's method.

I. 0.21172 gram of the substance gave 0.34615 gram of carbon dioxide and 0.08958 gram of water.

II. 0.18255 gram of the substance gave 0.29735 gram of carbon dioxide and 0.08292 gram of water.

For $C_7H_9SNO_3$:

		Theory.	Found. I.	II.
C_7	83.79	44.89	44.58	44.41
H_9	9.00	4.82	4.71	5.15
S	31.98	17.13	17.10	17.23
N	14.01	7.51	7.26	7.58
O_3	47.88	25.65		
	186.66	100.00		

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[1] Messrs. Hunter and Collier kindly made these determinations for me.

The compound is, therefore, methoxybenzenesulphonamide, and since it is obtained from sulphanilic acid in which the amido and sulphonic acid groups are in the para position, it is para-methoxybenzenesulphonamide.

Besides the methoxy compound there is also formed benzene-sulphonic acid. Consequently the product obtained from the decomposition of the diazo compound is a mixture. Since the amides of these two acids are well crystallized substances, an attempt was made to separate them by fractional crystallization, in order to form a definite idea as to the relative quantities formed in the decomposition. This attempt was unsuccessful, owing to the fact that both amides are about equally soluble in water, alcohol, ether, and mixtures of alcohol and water in various proportions. The following experiments were made with the object of finding a method for separating the two acids :

A quantity of the diazo compound was decomposed with methyl alcohol at a pressure of 760–780 mm. of mercury. After the reaction was completed, the excess of alcohol was distilled off, the syrupy residue diluted with water and treated with animal char-coal. A portion of this product was neutralized with barium carbonate. The solution of the barium salts was evaporated to dryness and the residue boiled with alcohol. A portion dissolved.

Analysis of the portion soluble in alcohol :

0.1713 gram of the substance gave 0.0825 gram of barium sul-phate, corresponding to 28.33 per cent. of barium. The theoreti-cal per cent. of barium in barium methoxybenzenesulphonate is 26.83, and in barium benzenesulphonate, 30.40.

Analysis of portion insoluble in alcohol :

0.12275 gram of the substance gave 0.0574 gram of barium sulphate, corresponding to 27.50 per cent. of barium. Similar experiments were made, using methyl alcohol as the solvent, with the following results :

0.15112 gram of the substance soluble in methyl alcohol gave 0.074 gram of barium sulphate, corresponding to 28.80 per cent. of barium.

0.14215 gram of the substance insoluble in methyl alcohol gave 0.07071 gram of barium sulphate, corresponding to 29.26 per cent. of barium.

It is evident from these results that the barium salts cannot be separated in this way.

Attempts to separate the two Acids by means of the Anilides.—
Aniline was added slowly to the chlorides ; action took place with
evolution of heat. The anilides thus obtained were washed with
dilute hydrochloric acid, and afterward with a *small* quantity of
caustic soda. Care must be taken not to use too much of this
reagent, as it dissolves the anilides. Water is used to remove the
caustic soda. The anilides were then crystallized from water, or
preferably, from a mixture of equal parts of water and alcohol.
Two kinds of crystals were deposited, small needles and irregular
shaped plates, but I was unable to obtain a satisfactory separation
in this way.

The following salts of the two acids were then prepared :
barium, sodium, ammonium, potassium, calcium, silver, lead,
copper, and zinc.

The barium, calcium, lead, and zinc salts were prepared by
neutralizing the acids with the corresponding carbonates. The
sodium, ammonium, and potassium salts were made from the
barium salts by precipitating the barium as carbonate ; the
copper[1] and silver salts by precipitating the barium salts with the
corresponding sulphates. It was found impossible to separate
satisfactorily any of these salts by fractional crystallization.

An attempt was then made to obtain an idea of the relative
amounts of the two acids formed in the decomposition of the
diazo compound with methyl alcohol, by converting the products
into the barium salts, determining the percentage of barium in
the mixture of the two, and upon the basis of the results thus
obtained to draw a conclusion as regards the relative quantities
of the different acids obtained in the decomposition. With this
object in view I made the following barium determinations :

I. 0.07865 gram of the barium salts gave 0.03675 gram of barium
sulphate, corresponding to 27.48 per cent. of barium.

II. 0.1174 gram of the barium salts gave 0.05485 gram of barium
sulphate, corresponding to 27.47 per cent. of barium.

III. 0.13885 gram of the barium salts gave 0.0645 gram of
barium sulphate, corresponding to 27.32 per cent. of barium.

Six determinations of this kind were made, but, owing to vari-
ations in the results, not due to errors of analysis, no satisfactory
conclusions could be drawn. Owing to a lack of time I was unable
to continue experimenting along this line, and in consequence a

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[1] Freund : Ann. Chem. (Liebig) **120**, 80.

method for the separation of the products of the decomposition of the diazo compound with methyl alcohol has not been found. However, the following experiments will show conclusively the conditions favorable for the formation of the methoxy compound.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 850 mm. of Mercury.

26 grams of the diazo compound and 520 cc. of methyl alcohol, distilled from lime. were placed in the pressure-flask. Heat was applied until a pressure of 850 mm. (the highest pressure that could be obtained with the apparatus used) was indicated by the manometer. The decomposition was complete in two and a half hours. The alcohol was then distilled off and the dark red liquid residue treated with animal charcoal. It was then converted into the amides as above described. Only a partial separation of the amides could be effected, but it was sufficiently complete to show the presence of the paramethoxybenzenesulphonamide in larger quantities than the benzenesulphonamide.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 360 mm.

26 grams of the diazo compound and 520 cc. methyl alcohol were placed in the flask and heated until the pressure indicated was 340–360 mm. The experiment was carried out as above. The decomposition was much slower, the time required being a little more than five hours. The products of decomposition were transformed into the amides. The quantities of the methoxy- and hydrogen-amides were about equal.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at Ordinary Pressure.

10 grams of the diazo compound and 200 cc. methyl alcohol were placed in a flask to which was attached an inverted condenser. The flask was heated on a water-bath. The action took place slowly and was complete in three hours. The products of decomposition were treated as above. Two amides were obtained, the hydrogen-amide being present in larger quantity than the methoxy-amide.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at Diminished Pressure.

The apparatus used in this experiment was devised by Mr. R. M. Parks, of this laboratory, and used by him in his study of the action of methyl alcohol on paradiazoorthotoluenesulphonic acid.[1] It is very simple and answers the purpose for which it is intended, admirably.

10 grams of the diazo compound and 200 cc. methyl alcohol were placed in the flask, which was heated on a water-bath. The experiment was conducted in the ordinary way, the pressure being 450 mm. less than the atmospheric pressure. Eight hours were required to effect complete decomposition. The product was converted into the amide. But *one* amide was formed, the melting-point of which (154°) was that of benzenesulphonamide, showing that the hydrogen reaction only took place.

These experiments led to the conclusion that if a sufficiently high pressure could be obtained, the decomposition would result in the formation of the methoxy compound only. With this object in view I made the next experiment.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 30 Atmospheres.

1 gram of the diazo compound and 10 cc. methyl alcohol were placed in a hard-glass tube, which was then sealed. It was heated for two hours at a temperature of 160° in a Carius furnace. The reaction took place readily, a dark red liquid being formed. The pressure in the tube, calculated from the vapor tension of methyl alcohol at 160°, was at least 30 atmospheres The decomposition probably takes place at a pressure much lower than this. The product of the decomposition was converted into the amide, which was found to be the *methoxy* amide. This was the *only* amide formed.

This experiment completes the chain of evidence showing that low pressure favors the hydrogen reaction and high pressure the methoxy reaction. This is in accordance with the results obtained in previous investigations carried on in this laboratory. Having arrived at these results with methyl alcohol, the idea of investigating the action of ethyl and propyl alcohols under the same conditions naturally presented itself.

[1] This Journal **15**, 320.

Action of Ethyl Alcohol on Paradiazobenzenesulphonic Acid at Ordinary Pressure.

For this and the succeeding experiments with this alcohol, ethyl alcohol of 95 per cent., distilled from lime, was used. 10 grams of the diazo compound and 200 cc. of ethyl alcohol were placed in a balloon flask, to which was attached an inverted condenser. Upon applying heat the alcohol assumed a yellow color, which gradually passed through pink to a deep red. The odor of aldehyde was plainly perceptible during the course of the experiment. About two hours were required for complete decomposition. The deep red liquid was then freed from the alcohol, which remained unacted upon, and after purification with animal charcoal was converted into the amide. But *one* amide was found, and its crystal form and melting-point showed it to be benzenesulphonamide.

Action of Ethyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 350 mm.

10 grams of the diazo compound and 200 cc. ethyl alcohol were placed in the pressure-flask. Heat was applied until a pressure of 350 mm. was indicated by the manometer. The pressure was held at this point until the decomposition was complete, one and a half hours being required for this purpose. The product of decomposition was treated as before and converted into the amide. Only *one* amide was formed, and this was benzenesulphonamide.

Action of Ethyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 840 mm.

10 grams of the diazo compound and 200 cc. ethyl alcohol were placed in the pressure-flask. The decomposition took place at a pressure of 820–840 mm., about seventy minutes being required for complete decomposition. The product was converted into the amide as above. Only *one* amide was found. This was benzene-sulphonamide.

These experiments show that when ethyl alcohol acts upon diazobenzenesulphonic acid under the varying conditions of pressure given above, the ethoxy reaction does not take place. Ador and Victor Meyer decomposed diazobenzenesulphonic acid with ethyl alcohol about twenty years ago.[1] They found only the hydrogen product.

[1] Ann. Chem. (Liebig) **159**, 8.

Action of Propyl Alcohol on Paradiazobenzenesulphonic Acid at Ordinary Pressure.

5 grams of the diazo compound and 50 cc. propyl alcohol, boiling-point 96°, were placed in a small flask connected with an inverted condenser. The flask was placed in a bath of a concentrated solution of sodium chloride. The bath was heated to boiling for two hours. The decomposition may have been complete, and probably was, before this time, but owing to the fact that the diazo compound contained some sulphanilic acid which had escaped the diazotizing action, and that the product of the decomposition was a black tarry liquid, it was difficult to tell accurately when the decomposition was complete. The excess of propyl alcohol was distilled off, the tarry residue diluted with water and filtered. The solution filtered with great difficulty, and a residue was left on the filter which was not sulphanilic acid. The filtrate was a muddy-looking liquid, holding something in suspension which could be removed only by repeated filtering. Upon adding a solution of barium hydroxide to neutralize the acid or acids formed, and to precipitate the sulphuric acid formed from the decomposition of the sulphonic acid, a tarry deposit was obtained. This was filtered off, and carbon dioxide passed into the solution to precipitate the excess of barium hydroxide. The barium carbonate was then filtered off and the solution boiled to decompose any acid barium carbonate which might have been formed. Sodium carbonate was then added, and after filtering, the solution was evaporated to dryness. The sodium salt was of a dark brown color. This was treated with phosphorus pentachloride. The residue obtained after driving off the phosphorus oxychloride was a black oily liquid weighing 2 grams. This was treated with an excess of concentrated ammonium hydroxide. After evaporating off the excess, a black gummy substance was obtained. This was dissolved in hot water and treated with animal charcoal, small quantities only being used. It did not crystallize well from water; mixed with small white crystals there was always found a dark gummy substance. This mixture was recrystallized from alcohol, the alcohol removed, and the crystals redissolved in hot water. By this means they can be obtained pure. An examination showed them to be the crystals of benzenesulphonamide. No other amide was found.

When paradiazobenzenesulphonic acid is decomposed with propyl alcohol, a much more serious breaking down occurs than when the decomposition is effected with either methyl or ethyl alcohol. The amide, or rather the acid from which the amide is derived, can be obtained only in very small quantities, while the principal product of the decomposition, so far as quantity is concerned, is the tarry matter referred to above.

Action of Propyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 700 mm.

The object of this experiment was to determine what effect a higher pressure than that used in the preceding experiment would have on the decomposition products. I desired to effect the decomposition at a pressure of about 840 mm. The experiment was carried out in the usual way. Upon applying heat the decomposition began almost immediately, and before the pressure could be raised to 840 mm. it was complete, the manometer indicating 700 mm. The product of this action was a black tarry liquid. It was purified with animal charcoal, then treated with barium hydroxide and converted into the amide as above. But *one* amide, benzenesulphonamide, was formed, and that in very small quantity.

The results obtained with ethyl and propyl alcohols are in accordance with those on record. Experiments with other alcohols were not made, the results obtained being considered sufficient for the purposes of this investigation.

The acid of which methoxybenzenesulphonamide is a derivative has been prepared by Kekulé,[1] and by Cahours and Annaheim;[2] and some of its derivatives by Haitinger.[3] I desired to prepare the acid in the manner described by Kekulé from anisol (methyl-phenyl ether) and sulphuric acid, in order that the amide made from it might be compared with the amide obtained from the acid formed by the decomposition of diazobenzenesulphonic acid with the methyl alcohol.

Preparation of Anisol.—In view of the observations of Remsen and Orndorff[4] that phenetol is the principal product of the action of ethyl alcohol on diazobenzene nitrate, it was thought probable that anisol would be formed by the action of methyl alcohol.

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[1] Ztschr. f. Chem. **1867**, 201.
[3] Ann. Chem. (Liebig) **172**, 47.
[2] Monatshefte **4**, 173.
[4] This Journal **9**, 387.

This was found to be the case, and indeed the method can be recommended for the preparation of anisol.

The diazo compound and absolute methyl alcohol were heated together in a flask connected with an inverted condenser. The decomposition began almost immediately, and after the temperature had been raised to 45° the burner was removed. The decomposition continued without further application of heat. I afterwards found that the decomposition will take place as well without the application of heat. If methyl alcohol and diazobenzene nitrate be brought together and allowed to stand, decomposition begins in 10–15 minutes, with elevation of temperature. After the action was complete the contents of the flask were subjected to distillation. Anisol and methyl alcohol passed over. The alcohol had a yellow color and an aromatic odor, due to the presence of anisol. This distillate was treated with about six times its volume of a saturated solution of sodium chloride. On standing, a light yellow oil collected at the surface. In order to obtain the last portions of anisol, the sodium-chloride solution was distilled ; methyl alcohol and a small quantity of anisol passed over, but in this case the oil collected in the bottom of the receiver in globules and could easily be obtained. To the contents of the flask from which the anisol and methyl alcohol had been obtained in the first instance, sodium hydroxide was added to alkaline reaction. The flask was then heated and steam passed into it, when a small quantity of anisol passed over with the water vapor. Sulphuric acid was then added to the mixture in the flask to acid reaction and it was again subjected to distillation with steam. Orthonitrophenol was formed in the receiver and condenser. The residue in the flask was not examined further. The anisol obtained was purified by treating with fused calcium chloride and then distilled. It boiled at 151°.

Action of Sulphuric Acid on Anisol.—The anisol was poured slowly into an excess of ordinary concentrated sulphuric acid. It apparently dissolved, with a slight elevation of the temperature of the mass. It was then heated for half an hour on the water-bath. The mixture was neutralized with barium carbonate and converted into the potassium salt. This solution was evaporated to dryness. The dried substance is exceedingly hard, brittle and hygroscopic. To preserve it in the dry condition it must be kept in a desiccator. This potassium salt was converted into the sulphonic chloride by treatment with phosphorus pentachloride. At the ordinary tem-

perature no action takes place, and it is necessary to apply heat. After distilling off the phosphorus oxychloride the residue was treated with water. No oil was observed. I then added ether in order to extract any sulphonic chloride which might have been formed. Upon pouring off the ethereal solution and distilling, beautiful crystal plates, of a pleasant odor, somewhat suggestive of the sulphonic chlorides in general, were obtained. These were supposed to be the crystals of either ortho- or paraanisolsulphonic chloride. The orthochloride melts at 55° (Haitinger). The crystals that I obtained melted at 86°. The following analysis of the compound was then made:

I. .10825 gram of the substance gave .1023 gram of silver chloride, corresponding to 23.37 per cent. of chlorine.

II. .23469 gram of the substance gave .21665 gram of silver chloride, corresponding to 22.83 per cent. of chlorine (Carius' method).

I. .2184 gram of the substance gave .2244 gram of carbon dioxide, corresponding to 28.02 per cent. of carbon.

II. .2880 gram of the substance gave .0694 gram of water, corresponding to 2.67 per cent. of hydrogen.

I. .23469 gram of the substance gave .3623 gram of barium sulphate, corresponding to 21.21 per cent. of sulphur (Carius' method).

For $C_6H_4.OCH_3.SO_2Cl$:

		Theory.	I.	II.
C_7	83.79	40.60	28.02	...
H_7	7.00	3.39	...	2.67
O_3	47.88	...	...	...
S	31.98	15.52	21.21	...
Cl	35.37	17.17	23.37	22.83

206.02

Evidently the compound analyzed was not anisolmonosulphonic chloride. It was the disulphonic chloride. This result was unexpected, since Zervas,[1] in order to make the disulphonic acid, treated anisol with *fuming* sulphuric acid. I obtained it as described above by using ordinary concentrated acid and heating for a half-hour on the water-bath.

·Analysis for $C_6H_3.OCH_3(SO_2Cl)_2$:

[1] Ann. Chem. (Liebig) **103**, 342.

		Theory.	I.	Found. II.
C₇	83.79	27.54	28.02	...
H₆	6.00	1.97	...	2.67
O₅	79.80	...	...	...
S₂	63.96	21.02	21.21	...
Cl₂	70.74	23.25	23.37	22.83

304.29

Lack of time prevented me from repeating the experiment with anisol and sulphuric acid. A portion of the disulphonic chloride obtained as described above was converted into the amide by treatment with ammonium hydroxide. Upon crystallizing the product, apparently crystals of two different kinds were found. They were not investigated.

Wichelhaus[1] states that if benzenesulphonamide be warmed with phosphorus pentachloride, benzenesulphondichlorphosphamide is formed. It was desirable to know how methoxybenzenesulphonamide would act under similar conditions. The following experiment was made to determine this action:

Two grams of methoxybenzenesulphonamide were treated with the proper proportion of phosphorus pentachloride. No action took place at the ordinary temperature. Upon applying heat, action began at once, and hydrochloric acid was given off. The oily product obtained was poured on a porous plate and allowed to stand over sulphuric acid for about two weeks (Wichelhaus). It was then dissolved in anhydrous ether and allowed to stand. Although several attempts were made to obtain crystals, they were unsuccessful. When the ether was allowed to evaporate off slowly, a clear viscous liquid was obtained, which, upon being exposed to the air, gave off hydrochloric acid. When the product of the decomposition of the amide and phosphorus pentachloride was allowed to stand in moist air, or when water was added to it, decomposition began at once and the substance was converted back to the amide. In this respect its behavior is similar to that of benzenedichlorphosphamide.

Action of Nitric Acid on Methoxybenzenesulphonamide. — 4.7 grams of methoxybenzenesulphonamide were added slowly to 15 cc. of fuming nitric acid. The action was very energetic. For this reason only a small quantity of the amide should be added at a time. Upon diluting the nitric acid solution with water

[1] Ber. d. chem. Gesell. **2,** 502.

a precipitate or emulsion of minute globules of oil was obtained. The solution was diluted still further and heated to boiling. The oil dissolved with difficulty. Upon cooling, beautiful crystals of slender needle-shape, somewhat similar to those of the amide, separated. A determination of the melting-point, which was found to be 88°, showed that the substance was not the amide. A test for sulphur failed to show its presence. This, together with the form of the crystals, led me to believe that the substance was metadinitrobenzene, and this proved to be the case.

The melting-point was 88° (uncorrected). That of metadinitrobenzene is 89.9° (corrected).[1] Its solubility in hot water, alcohol and ether agreed with that of metadinitrobenzene in these reagents.

The preceding experiment was repeated, a more dilute acid— ordinary concentrated nitric acid—being employed. The action was not quite so energetic, but otherwise the same results were obtained. With more dilute acid the reaction does not take place. The amide dissolves, but, on cooling, it crystallizes out unchanged. These experiments show that the paramethoxybenzenesulphonamide is very susceptible to the action of nitric acid. Not only are the methoxy and sulphonamide groups, which are in the para position, replaced by the nitro group, but apparently a rearrangement of the parts takes place, the nitro groups entering the *meta* position.

Summary of Results.

I. When paradiazobenzenesulphonic acid is decomposed with methyl alcohol under diminished pressure, only the hydrogen product is obtained.

II. At ordinary pressure both the hydrogen and methoxy reactions take place.

III. At a pressure of 350 mm. both reactions take place.

IV. At a pressure of 850 mm. both reactions take place, the methoxy compound predominating.

V. At a pressure of about 30 atmospheres the methoxy reaction alone takes place.

VI. When ethyl alcohol is used in the decomposition of paradiazobenzenesulphonic acid, at various pressures up to 850 mm., only the hydrogen product is obtained.

VII. When propyl alcohol is used under the same conditions the hydrogen product only is formed.

[1] Griess : Berichte **11**, 625.

THE PROTEIDS OF THE WHEAT KERNEL.

By Thomas B. Osborne and Clark G. Voorhees.

Wheat flour has for centuries formed one of the most important articles of food for man, in consequence of the peculiar property which it possesses, in common only with rye flour, of forming a dough when mixed with water which on leavening and baking produces a light, porous bread. This characteristic depends wholly on the proteid constituents of the seed.

The characters, composition, and even the number of the proteids contained in the wheat kernel or derived from it, are the subject of very conflicting statements on the part of those who have investigated these bodies. It was with a hope of clearing away much of the existing confusion, by applying the modern methods of study, that this investigation was undertaken. The amount of work involved has been very great, and consequently its record is long ; but it was deemed best to publish the results in full detail, as otherwise a clear comprehension of what we have done and the value of our conclusions would be impaired.

I.—Historical.

Beccari[1] appears to have been the first to publish the fact that by washing with water a dough made of wheat flour, as long as starch is removed, a coherent, elastic mass is obtained.

Einhof[2] found that hot alcohol extracts from wheat flour a substance which is precipitated by cooling, by dilution, or by concentration. This he considered to be the same substance as the gluten (*Kleber*) obtained by washing the flour with water.

Taddei[3] found that on boiling gluten with alcohol a part is dissolved. The residue left by thus treating the gluten he named *zymom ;* the part soluble in alcohol, *gliadin.*

Berzelius[4] believed to have found in the alcoholic extract of the gluten another proteid substance which he called mucin. This was obtained by treating the proteid extracted by alcohol from gluten with acetic acid, the mucin remaining as a jelly undissolved. Berzelius[5] considered that Taddei's zymom and gliadin were

[1] Common. Bonon. **1**, 1, 122.

[2] Jour. d. Chemie von Gehlen **5**, 131, 1805.

[3] Annals of Phil., May, 1820, and Abstract, Schweiger's Jour. f. Chem. u. Physik. **29**, 514.

[4] Lehrbuch d. Chemie, 3. Aufl. **6**, 453.

[5] Berzelius Jahresb. **7**, 231, 1826.

substances already known, that the gliadin was identical with the body obtained by Einhof from wheat, rye, and barley. His own investigation also indicated that Taddei had applied new names to known and common constituents of seeds. By diluting the alcoholic extract of gluten with water and concentrating, a substance separated on cooling the residual aqueous solution, having the same nature as that separated by Einhof in a similar way from rye and barley. The substance undissolved by alcohol Berzelius found to be so similar to animal albumin that the two could not be distinguished in appearance, and therefore called it *plant albumin.*

De Saussure [1] found wheat gluten to contain about 72 per cent. of plant albumin in the insoluble form, about 20 per cent. of plant gelatin, or as he proposed to call it, *glutin*, and about 1 per cent. of mucin.

This latter substance he regarded as similar to the mucin described by Berzelius, though prepared in a different manner. It was obtained by extracting the gluten with hot alcohol, separating the plant gelatin or glutin by adding an equal volume of water, and concentrating to one-sixth. On standing, and by repeatedly adding water and evaporating until the liquid remained clear on cooling, a solution was obtained which, evaporated to dryness, yielded mucin in an impure form.

This body De Saussure supposed had the power to convert starch into sugar.

Boussingault,[2] like Einhof, considered the portion of gluten soluble in alcohol to be the same as the entire gluten proteid. He gave analyses of four preparations: **1.** The washed gluten; **2.** The proteid extracted by alcohol; **3.** Preparation **2** dissolved in acetic acid and precipitated by carbonate of ammonia; **4.** Albumin coagulated by heating the water-washings of the gluten after the starch had been separated.

	1	2	3	4
Carbon	53.5	54.2	52.3	52.7
Hydrogen	7.0	7.5	6.5	6.9
Nitrogen	15.0	13.9	18.9	18.4
Oxygen	24.5	24.4	22.3	22.0
	100.0	100.0	100.0	100.0

[1] Schweiger's Jour. **69**, 188, 1833.

[2] Ann. de chim. et de phys. **65**, 30. Abstract, Berzelius Jahresb. **18**, 327, 1837.

Berzelius, commenting on the above analyses, remarked that the lower content of nitrogen in **2** as compared with **3** shows that the mucin which is contained in it has a lower nitrogen content than plant gelatin, and that Boussingault evidently did not know of the existence of mucin.

Liebig,[1] in a paper on the nitrogenous food substances of the vegetable kingdom, discussed the relation of vegetable proteids to those of animal origin. In wheat gluten he found a substance insoluble in alcohol, Taddei's zymom and Berzelius' plant albumin, which he named plant fibrin, on account of its agreement both in composition and properties with blood fibrin. He rejected Berzelius' name of plant albumin, as solubility in water is an essential characteristic of albumins. The substance extracted from the gluten by alcohol he called plant gelatin, and considered it to be a casein-like compound of a proteid with an organic acid, whose nature, however, he was unable to discover. He mentioned De Saussure's mucin, saying that its composition must be nearly the same as that of plant fibrin, since the composition of the crude gluten varied little from that of plant fibrin and albumin. The aqueous extract of the flour also contained albumin. He then gave the following analyses of these various substances, made in his laboratory by Jones, Will and Verentrap, and Scherer.

Plant Albumin.

	From Wheat.	From Plant Gelatin. Will & Verentrap.
Carbon	55.01	54.85
Hydrogen	7.23	6.98
Nitrogen	15.92	15.88
Oxygen		
Sulphur	21.84	22.39
Phosphorus		
	100.00	100.00

Plant Gelatin.

	Jones. Crude.	Extracted with Ether.	Ditto. purified.
Carbon	58.45	56.80	55.22
Hydrogen	7.65	7.60	7.42
Nitrogen	..	..	15.98
Oxygen	..	..	21.38
			100.00

[1] Ann. der Chem. u. Pharm. **39**, 129, 1841.

Plant Fibrin.

	Jones.	Scherer.	
Carbon	53.83	54.603	54.603
Hydrogen	7.02	7.302	7.491
Nitrogen	15.59	15.810	15.810
Oxygen			
Sulphur	23.56	22.285	22.096
Phosphorus			
	100.00	100.00	100.00

In these analyses, nitrogen was determined by finding the ratio of nitrogen to carbonic acid in the products of combustion, and then calculating the percentage of nitrogen from that of the carbon. Scherer[1] prepared plant fibrin by dissolving gluten in dilute potash water, filtering, neutralizing with acetic acid, extracting the precipitate with boiling alcohol as long as anything was removed, exhausting with ether and drying at 100°. The analysis of the preparation thus obtained, after recalculating the figures given by Scherer for the present atomic weight of carbon, was as follows :

Carbon	53.24
Hydrogen	7.13
Nitrogen	15.36
Sulphur	
Oxygen	25.17
Phosphorus	
	100.00

Bouchardat[2] considered wheat gluten to contain a body, named by him albuminose, which he described as a substance soluble in extremely dilute acids, forming the chief constituent of egg albumin, blood fibrin, casein, and grain gluten.

Dumas and Cahours[3] found four proteid substances in flour. After extracting gluten with alcohol, a gray, fibrous residue was obtained, which one of the authors had previously designated in 1839 as plant fibrin. The alcoholic solution on cooling deposited a proteid having the characteristics of casein. From the remaining solution, after concentration and cooling, a substance separated which they, like De Saussure, called *glutin.*

The aqueous solution obtained in washing out the gluten contained a body similar to albumin.

The fibrin, they say, had up to that time been considered as coagulated albumin, and the same composition had been assigned

[1]Ann. d. Chem. u. Pharm. **40**, 7, 1841.   [2]*Ibid.* **43**, 124, 1842.
[3]Jour. f. prakt. Chem. **28**, 398, 1843.

to both.   They found by careful analysis that the two bodies had
a different composition.   The fibrin freed from all substances
soluble in alcohol and ether, soaked in water, and treated with
diastase, to remove starch, had the following composition:

	1.	2.
Carbon	53.23	53.37
Hydrogen	7.01	7.02
Nitrogen	16.41	16.00
Oxygen, etc.	23.35	23.61
	100.00	100.00
Ash	1.06	

In this analysis nitrogen was determined by Dumas' method, and
carbon and hydrogen calculated for an atomic weight of 12.

As this analysis gave nearly the same composition as blood
fibrin, the authors considered the two bodies to be identical.

They obtained coagulated albumin by boiling and concentrating
the aqueous washings of the gluten.   After treating the coagulum
with diastase and extracting with alcohol and ether, it was dried
at 140° and analyzed.   Its composition was thus found to be:

Carbon	53.74
Hydrogen	7.11
Nitrogen	15.65
Oxygen, etc.	23.50
	100.00
Ash	8.50

This analysis, they said, shows that the albumin is identical with
egg albumin.   They found, however, that on prolonged boiling
the fibrin yielded a substance of the same composition as coagu-
lated albumin, and they therefore assumed that by heating with
water, albumin was split off from the fibrin and coagulated.

They then suggested that the albumin may have resulted from
a decomposition of the fibrin which had dissolved on washing out
the gluten.

The casein obtained by cooling the weak alcohol extract of the
gluten, after washing with water, alcohol and ether, and drying *in
vacuo*, gave the following results on analysis:

Carbon	53.46
Hydrogen	7.13
Nitrogen	16.04
Oxyen, etc.	23.37
	100.00

The proteid, called by the authors glutin, remaining in the alcoholic solution after deposition of the casein, was separated from solution by concentration to small volume, and, after drying, extracted with ether. When dried *in vacuo* at 140° they found it contained :

Carbon	53.27
Hydrogen	7.17
Nitrogen	15.94
Oxygen, etc.	23.62
	100.00

This, they claimed, showed the glutin to be isomeric with albumin and casein.

Mulder[1] extracted plant gelatin from gluten by means of alcohol. The solution was filtered hot, allowed to cool, and the white, flocculent precipitate which deposited was again dissolved in alcohol and twice separated by cooling, filtered off, extracted with ether, dried, and analyzed with the following result :

	I.	II.
Carbon	54.94	54.75
Hydrogen	7.11	6.99
Nitrogen	15.71	15.71
Sulphur	0.57	0.62
Oxygen	21.68	21.93
	100.00	100.00

This plant gelatin he considered to be a compound of sulphur with "protein," containing the same proportion of sulphur as blood albumin.

Von Bibra[2] states that by boiling gluten with diluted alcohol, insoluble plant fibrin remains undissolved, while plant gelatin and plant casein go into solution, the latter separating on cooling. These three bodies he found, after examining seven different samples of gluten, to be present in the following average proportions :

Plant fibrin	70.80
Plant gelatin	16.22
Plant casein	7.10
Fat	5.88
	100.00

[1] Ann. d. Chem. u. Pharm. **52.** 419, 1844.   [2] Die Getreidearten u. das Brod, 1860.

He assigns the following composition to each of these proteids :

	Plant Fibrin.	Plant Gelatin.	Plant Casein.
Carbon	53.57	53.57	54.88
Hydrogen	6.95	7.12	7.05
Nitrogen	15.70	15.57	15.71
Sulphur	1.02	0.88	0.76
Oxygen	22.76	22.86	21.60
	100.00	100.00	100.00

Von Bibra considers these bodies to have the same elementary composition and to be "isomers in the narrower sense of the term."

In the water used for washing out the gluten he found a coagulable proteid which he calls albumin. Dried at 110°, this coagulated proteid formed 1.34 per cent. of the flour and contained 15.65 per cent. of nitrogen.

Günsberg[1] found that on boiling gluten or plant gelatin with water a considerable part dissolved, which on cooling mostly separated. He says that the body previously called plant casein is a mixture of plant gelatin with the insoluble part of the gluten which has escaped separation on filtering, and that Taddei's view is correct that there are but two bodies contained in gluten. By boiling gluten with water he obtained five preparations, the average of whose composition was as follows :

Carbon	52.68
Hydrogen	6.77
Nitrogen	17.76
Oxygen	22.79
	100.00

In the same way from gliadin he obtained a body of the same composition, namely,

Carbon	52.65
Hydrogen	6.88
Nitrogen	17.45
Oxygen	23.02
	100.00

Commaille[2] recognized as proteid constituents of flour : 1. sitosin, soluble in water and coagulable by heat ; 2. imesin, dissolving

[1] Jour. f. prakt. Chem. **85,** 213, 1862.　　　　[2] J. Pharm. (4) **4,** 108, 1866.

after drying only in water containing 0.1 per cent. hydrochloric acid ; 3. sitesin, dissolving in water containing 0.1 per cent. hydrochloric acid ; 4. glutin, nearly insoluble in acidulated water, sparingly soluble in acetic acid, easily in strong acid, not miscible with water, forming an emulsion with alcohol which is separated by a large quantity of water and also by ether. Thus precipitated it dries to a translucent, white, friable mass slightly soluble in water. 5. Mucin, dissolves easily, even after drying, in water and cold alcohol of 80 per cent.

Ritthausen[1] recognizes five proteids in wheat, namely, gluten casein, gluten fibrin, plant gelatin or gliadin, mucedin, and albumin. The existence of the latter he considers somewhat doubtful, as it may possibly be a mixture of mucedin and gliadin. He formerly[2] considered Dumas' casein, or as he proposed to call it paracasein, to be a constituent of the gluten. The four bodies first named form the gluten, the first being insoluble in cold dilute alcohol, the others soluble in that menstruum. The albumin he obtains from the water used in washing out the gluten, by acidifying slightly with nitric acid and boiling. The gluten casein he prepared by thoroughly extracting the gluten with dilute alcohol, dissolving the residue in dilute potash water, precipitating with acetic acid, extracting the washed precipitate with dilute alcohol, redissolving the precipitate in dilute potash water, filtering, and again precipitating with acid.

The bodies soluble in alcohol are separated from each other by fractional precipitation from alcoholic or acetic-acid solution, the precipitations being repeated until the products have a constant composition as follows :

	Gluten Casein.	Gluten Fibrin.	Gliadin.	Mucedin.	Albumin.
Carbon	52.94	54.31	52.76	54.11	53.12
Hydrogen	7.04	7.18	7.10	6.90	7.18
Nitrogen	17.14	16.89	18.01	16.63	17.60
Sulphur	0.96	1.01	0.85	0.88	1.55
Oxygen	21.92	20.61	21.37	21.48	20.55
	100.00	100.00	100.00	100.00	100.00

Weyl and Bischoff[3] consider that the proteid matter of wheat is chiefly a myosin-like globulin which they call vegetable myosin,

[1] Die Eiweisskorper, etc. Bonn, 1872.   [2] J. prakt. Chem. **85**, 193.
[3] Ber. d. deutsch. chem. Gesell. 1880, 367.

and that if so, this must be the substance from which gluten is derived, for other proteids are present only in small quantity. Extraction with 15-per cent. salt solution left a residue from which they obtained no gluten. They therefore considered it probable that the gluten forms from the myosin in consequence of a ferment action similarly to the formation of fibrin from fibrinogen. No ferment, however, could be detected. They also found that large amounts of sodium chloride, sodium sulphate and magnesium sulphate hindered the formation of gluten in the same way that sodium and magnesium sulphates hinder the formation of fibrin. As no gluten was obtained from flour extracted with alcohol, they concluded that the myosin had been coagulated. By warming flour 48–96 hours below 6°, the coagulation-point of myosin, no gluten was obtained from the meal after adding a little unwarmed flour, showing that the gluten-forming substance had been coagulated.

According to Martin,[1] alcohol extracts from gluten but one proteid substance. This is soluble in hot water, but insoluble in cold, hence is insoluble phytalbumose. The residue remaining after treatment with alcohol is uncoagulated proteid, soluble in dilute acids and alkalies; this he called gluten fibrin. The insoluble phytalbumose is not present as such in flour, since direct extraction of the meal with 75-per cent. alcohol removes no proteid. Extraction with water yields less globulin and soluble albumose than extraction with sodium-chloride solution of 10–15 per cent. Martin therefore concluded that the insoluble phytalbumose is formed from the soluble by the action of water, the gluten fibrin being formed by a similar action of water on the globulin, that is, conversion into an albuminate. This albuminate and the insoluble phytalbumose together constitute gluten.

W. Johannsen[2] believes that there is no ferment action in the formation of gluten. Dough was obtained by grinding dried gluten and mixing with starch, and also by mixing moist gluten with starch.

Chittenden and Smith[3] prepared many samples of gluten casein according to Ritthausen's method. As an average of eight analyses they give the following composition:

[1] British Medical Jour. **2**, 104, 1886.

[2] Ann. Agromom. **14**, 420, 1888. Abstract, Jour. Chem. Soc., March, 1889.

[3] Jour. Physiol. **11**, 419, 1890.

Carbon	52.87
Hydrogen	6.99
Nitrogen	15.86
Sulphur	1.17
Oxygen	23.11
	100.00

The wheat used in the work now to be described was of two kinds. One of these, Scotch Fife, a spring wheat, was obtained through the kindness of Dr. D. N. Harper, late Chemist of the Minnesota Experiment Station. It was carefully selected, free from all other varieties, and was milled under the supervision of Dr. Harper, who supplied us with samples of the various mill products, together with some of the unground wheat. Two grades of flour were used, namely, "patent flour," made from the finest and purest middlings, and "straight flour," from the coarser and less pure middlings. The "shorts," chiefly composed of the outer coating of the seeds together with adhering portions of the endosperm, was also examined. Samples of whole wheat flour were prepared as required from the wheat by grinding small quantities in the laboratory mill. The other wheat used was a variety of winter wheat known as "Fultz." This was procured from a seedsman, was carefully selected and freshly harvested. Portions of this wheat were ground in the laboratory mill as needed, and only whole wheat flour was obtained from this sample. Preliminary experiments showed that all these different flours yielded proteid matter to diluted alcohol, to water, to 10-per cent. sodium-chloride solution, and after complete and successive extraction with these several reagents, to dilute potash water. The bodies extracted by these reagents will now be considered separately.

II.—PROTEIDS SOLUBLE IN WATER.

a.—*Preliminary Experiments.*

200 grams of the "straight flour" from spring wheat were poured with constant stirring into 800 cc. of distilled water. No coherent gluten formed, the undissolved flour settling down as a loose mass. After a few hours' digestion the solution was filtered and the residue collected on a filter. When most of the solution had run off the residue began to form a tough, glutinous mass, which increased in density as the excess of solution separated.

The water-extract was of a straw-yellow color, becoming red-brown on standing, and had a *very* slight acid reaction.

Saturated with ammonium sulphate, a bulky precipitate formed, which on standing contracted, showing the solution to contain but a small amount of proteid matter. After 24 hours this precipitate was completely soluble in water, giving no evidence of the formation of so-called albuminates. Saturation with sodium chloride gave a small precipitate. Acetic acid in the cold gave no precipitate until sodium chloride was added.

On slowly heating the solution gave a turbidity at 48° and a flocculent coagulum at 52°. After heating to 65° for some time and filtering, the solution became turbid again at 73°, flocks forming in very small amount at 82°. No more separation occurred on further heating the extract even to boiling. The addition of a little acetic acid and sodium chloride gave a small precipitate. The body coagulating at 52° formed the greater part of the proteid in solution. The complete coagulation of this proteid was accomplished with difficulty, prolonged heating at 65° being necessary to cause it to separate completely. The addition of sodium chloride greatly facilitated the final coagulation. The temperature at which the flocculent coagulum separated depended upon the rate of heating. Unless the solution was heated very slowly, the point at which flocculation occurred was found to be much above 52°.

As the subsequent experiments showed that these same proteids went into solution on extracting the flour with 10-per cent. sodium-chloride brine, the further examination of the water-soluble substances was confined to extracts originally made with 10-per cent. sodium-chloride solution after separation of the globulins by dialysis.

Again, 4000 grams of straight flour were treated with 8 liters of 10-per cent. sodium-chloride solution, strained through a sieve to break up all lumps, and allowed to settle over night. Only about one-half the extract could be separated from the undissolved flour by decantation and filtration. The residue was stirred up with 2 liters more of the same solution, and again thrown on to filters. The filtrate was collected in successive portions and saturated with ammonium sulphate as fast as obtained. The precipitate so produced was filtered off, treated with 10-per cent. brine, the resulting solution filtered clear, and dialyzed until chlorides

were removed. The globulin which was thus precipitated was filtered off, and the solution again dialyzed for 14 days, but no more globulin could be obtained.

On slowly heating a portion of this solution in a double water-bath, turbidity occurred at 48°, flocks separating at 55°. After heating for some time at 65° the coagulum was filtered off and the solution again heated, a turbidity resulting at 70°, and a very minute amount of flocculent coagulum at 80°. Boiling the solution after filtering gave no more precipitate, and nothing was obtained by adding a *little* salt and acetic acid. If the amount of salt was increased and acetic acid added, a precipitate was obtained. Equal volumes of this solution were treated with 20 per cent. of sodium chloride and a little acetic acid. To the first the salt and acid were added directly, to the second after heating to 65° and filtering off the coagulum, and to the third after heating to 95° and likewise filtering. The first portion gave the most precipitate, the last the least, showing that the coagulable proteids are thus precipitated. The filtrate from the first portion when neutralized and boiled gave no precipitate, showing that the separation of the albumin was complete. This result was to be expected, for albumin may be thus precipitated by salt and acid.

This solution freed from globulins by dialysis gave a precipitate on saturation with sodium chloride, the filtrate from which became turbid when heated to 43°, flocculent at 56°, and no more precipitation on further heating, showing that the higher-coagulating proteid was thus removed. This dialyzed solution likewise gave a considerable precipitate with nitric acid. On heating a part remained insoluble, and on filtering this off the filtrate gave a precipitate on cooling, which dissolved again on heating and reappeared as often as the solution was cooled. The filtrate from the salt and acid precipitate did not give this reaction, but the solution of the precipitate in water gave it very strongly. This reaction is characteristic of some proteoses, and shows that the salt and acid precipitate contains a proteose together with the albumins. This proteose is likewise precipitated by saturating the extract with salt, for on dissolving the precipitate so produced, and separating the albumin contained in it by coagulation, the filtrate gave a strong *red* biuret reaction, and a heavy precipitate with nitric acid which dissolved on warming and precipitated again on cooling. The filtrate from the precipitate caused by saturation with salt gives

no reaction with nitric acid, showing that the proteose is thus completely precipitated.

Saturation of the solution with sodium chloride seems to render the higher-coagulating proteid insoluble, for an aqueous solution of the precipitate shows only the presence of the low-coagulating albumin, and the filtrate from the salt saturation precipitate likewise coagulates only at the lower temperature.

We are able then to recognize three distinct proteid substances soluble in pure water, namely, two coagulable, presumably both albumins, and a proteose. As it was found that the proteid removed from the flour by treatment with alcohol was to a slight extent soluble in pure water, it might be thought that one of these bodies was identical with that. The identity with the two albumins is excluded by the fact that they are precipitated by heat, and with the proteose by the fact that the alcohol-soluble proteid gives a precipitate with hydrochloric acid when dissolved in distilled water and also with a trace of sodium chloride, which the proteose does not.

In order to be sure that the body, which was apparently an albumin, was not a myosin-like globulin held in solution by the small amount of salts contained in the river water used for dialysis, as was suggested by its partial precipitation by saturation with sodium chloride, the following experiment was tried: 250 cc. of a strong aqueous extract of winter wheat meal was made and placed in a dialyzer immersed in distilled water. Distilled water was then allowed to run through the outer vessel continuously for 48 hours. A small precipitate was then formed, which was filtered off, the clear solution returned to the dialyzer, and the process continued for five days longer. No more substance separated. The entire solution, which was still found to coagulate at 54°, was then evaporated to dryness in a weighed platinum dish, the considerable proteid residue burned off, and the total mineral matter weighed. It was found to amount to only 0.0008 gram, thus proving that the substance was an albumin.

b.—*Albumins.*

The remainder of the foregoing dialyzed solution which was left after the preliminary trials preceding the last, formed about five-sixths of the whole. This was then heated in a large water-bath to a temperature not exceeding 61°, the water in the bath being

kept between 60° and 65°. After an hour the precipitate was filtered off, washed thoroughly with water, alcohol, absolute alcohol and ether, and dried. Before drying the coagulum was a white, voluminous, semi-solid mass, which when completely dried over sulphuric acid became dense and horny.

4.3 grams of this preparation were obtained, and after drying at 110° it was found to have the following composition:

COAGULATED WHEAT ALBUMIN. *Preparation* 1.

	I.	II.	Average.	Ash-free.
Carbon	53.04	53.28	53.16	53.27
Hydrogen	6.74	6.89	6.82	6.83
Nitrogen	16.86	16.95	16.91	16.95
Sulphur	1.27	..	1.27	1.27
Oxygen	..	..	..	21.68
Ash	0.22	..	..	..
				100.00

Ash.—0.6479 gram dried substance gave 0.0014 gram ash = 0.22 per cent.

Carbon and Hydrogen, I.—0.3570 gram dried substance gave 0.6943 gram CO_2 = 53.04 per cent. C, and 0.2765 gram H_2O = 6.74 per cent. H.

II.—0.4062 gram dried substance gave 0.7937 gram CO_2 = 53.28 per cent. C, and 0.2522 gram H_2O = 6.89 per cent. H.

Nitrogen, I.—0.3789 gram dried substance gave 51.14 cc. N at 5° (barometer 773 mm. at 23°) = 16.86 per cent. N.

II.—0.3764 gram dried substance gave 53.15 cc. N at 6° (barometer 745.3 mm. at 22°) = 16.95 per cent. N.

Sulphur.—0.8292 gram dried substance gave 0.0769 gram $BaSO_4$ = 1.27 per cent. S.

Another lot of 10,000 grams of flour was extracted with 10-per cent. sodium-chloride solution and treated in the same way as the extract last described. The albumin was obtained from the extract after completely removing the globulins, by coagulation at 60°. This coagulum was treated in the same manner as preparation 1. It weighed 6.4 grams and had the following composition:

COAGULATED WHEAT ALBUMIN. *Preparation* 2.

	I.	II.	Average.	Ash-free.
Carbon	52.91	52.98	52.95	53.06
Hydrogen	6.86	6.74	6.80	6.82
Nitrogen	16.93	17.01	16.97	17.01
Sulphur	1.28	1.31	1.30	1.30
Oxygen	..	..	..	21.81
Ash	0.22	..	..	..
				100.00

Ash.—0.6376 gram substance dried at 110° gave 0.0014 gram ash = 0.22 per cent.

Carbon and Hydrogen, I.—0.4020 gram dried substance gave 0.7800 gram CO_2 = 52.91 per cent. C, and 0.2482 gram H_2O = 6.86 per cent. H.

II.—0.3880 gram dried substance gave 0.7536 gram CO_2 = 52.98 per cent. C, and 0.2362 gram H_2O = 6.74 per cent. H.

Nitrogen, I.—0.3825 gram dried substance gave 54.16 cc. N at 11° (barometer 756 mm. at 22°) = 16.93 per cent. N.

II.—0.3015 gram dried substance gave 42.23 cc. N at 11° (barometer 768 mm. at 23°) = 17.01 per cent. N.

Sulphur, I.—0.6785 gram dried substance gave 0.0632 gram $BaSO_4$ = 1.28 per cent. S.

II.—0.3707 gram dried substance gave 0.0354 gram $BaSO_4$ = 1.31 per cent. S.

The filtrate from preparation **2** was then heated to 75° and a small amount of coagulum obtained which was highly colored. This was filtered off and washed with alcohol, thereby removing much of the color. After drying over sulphuric acid, 0.65 gram was obtained, which on analysis gave the following results:

COAGULATED WHEAT ALBUMIN. *Preparation* **3.**

		Ash-free.
Nitrogen	16.91	16.94
Ash	0.18	..

Ash.—0.2149 gram substance dried at 110° gave 0.0004 gram ash = 0.18 per cent.

Nitrogen.—0.3234 gram dried substance gave 45.05 cc. N at 11° (barometer 767.2 mm. at 22°) = 16.91 per cent. N.

Another preparation was made from the same flour by extracting 10,000 grams with 10-per cent. sodium-chloride solution, filtering the extract and dialyzing at once. In this case the precipitation of the proteids with ammonium sulphate was omitted. After complete dialysis the solution was filtered from the globulin which had separated, and the solution heated at once to 90°. This temperature was high enough to precipitate both albumins, but as the albumin coagulating at 75°–80° formed but a mere trace of coagulum, its separation was in this case not attempted.

Dried over sulphuric acid, this preparation, which in all respects resembled **1** and **2**, weighed 16.5 grams, and when analyzed gave the following results:

COAGULATED WHEAT ALBUMIN. *Preparation* 4.

	I.	II.	Average.	Ash-free
Carbon	52.86	..	52.86	53.02
Hydrogen	6.85	..	6.85	6.87
Nitrogen	16.21	16.20	16.21	16.26
Sulphur	1.20	..	1.20	1.20
Oxygen	..	..	..	22.65
Ash	0.32	..	0.32	..
				100.00

Ash.—0.5514 gram substance dried at 110° gave 0.0018 gram ash = 0.32 per cent.

Carbon and Hydrogen.—0.2918 gram dried substance gave 0.5656 gram CO_2 = 52.86 per cent. C, and 0.1800 gram H_2O = 6.86 per cent. H.

Nitrogen, I.—0.4049 gram dried substance gave 55.36 cc. N at 16° (barometer 763 mm. at 27°) = 16.21 per cent. N.

II.—0.3393 gram dried substance gave 46.07 cc. N at 16° (barometer 767.5 mm. at 23°) = 16.20 per cent. N.

Sulphur.—0.7326 gram dried substance gave 0.0643 gram $BaSO_4$ = 1.20 per cent. S.

Another preparation of albumin was made by extracting with 10-per cent. sodium-chloride solution 2000 grams of so-called "shorts" from the spring wheat flour. This substance consisted chiefly of particles of the outer coats of the seed to which more or less of the adjacent endosperm adhered. After three hours the extract was strained through a coarse cloth and squeezed out from the residue in a screw press. After the starch had settled, the nearly clear extract, which had a deep red-brown color, was syphoned off and saturated with ammonium sulphate. The precipitate thus produced was filtered off and dissolved in 10-per cent. sodium-chloride brine. The resulting solution filtered from all the insoluble matter was then dialyzed free from chlorides, the precipitated globulins filtered off, and the albumin contained in the solution separated by heating to 65°. The coagulum was then filtered off, washed with water, alcohol and ether, and dried at 110° for analysis. It was found to have the following composition:

COAGULATED WHEAT ALBUMIN. *Preparation* 5.

		Ash-free.
Carbon	52.36	52.71
Hydrogen	6.80	6.85
Nitrogen	16.62	16.73
Sulphur	1.34	1.34
Oxygen	..	22.37
Ash	0.67	..
		100.00

Ash.—0.3730 gram substance dried at 110° gave 0.0025 gram ash = 0.67 per cent.

Carbon and Hydrogen.—0.3067 gram dried substance gave 0.5889 gram $CO_2 = 52.36$ per cent. C, and 0.1870 gram $H_2O = 6.80$ per cent. H.

Nitrogen.—0.4305 gram dried substance gave 61.29 cc. at 19° (barometer 758.3 mm. at 23°) = 16.62 per cent. N.

Sulphur.—0.2314 gram dried substance gave 0.0225 gram $BaSO_4 = 1.34$ per cent. S.

Summary of Analyses of Coagulated Wheat Albumin.

	1.	2.	3.	4.	5.	Average.
C	53.27	53.06	..	53.02	52.71	53.02
H	6.83	6.82	..	6.87	6.85	6.84
N	16.95	17.01	16.94	16.26	16.83	16.80
S	1.27	1.30	..	1.20	1.34	1.28
O	21.68	21.81	..	22.65	22.27	22.06
	100.00	100.00		100.00	100.00	100.00

The agreement of these figures is satisfactory with the exception of the nitrogen in 4. The accuracy of this analysis in this respect, however, cannot be doubted, as four determinations of this element were made, all of which agreed closely. As this preparation was separated at a higher temperature than any of the others, it is possible that it had in consequence lost some of its nitrogen. So far as the writer can find, none of the analyses heretofore made which professed to give the composition of wheat albumin agree with the above, as shown by the following table:

Earlier Analyses of Wheat Albumin.

	Boussingault.	Jones.	Dumas and Cahours.	Adriani.	Ritthausen.
C	52.7	55.01	53.74	54.78	53.12
H	6.9	7.23	7.11	7.34	7.18
N	18.4	15.92	15.65	16.01	17.60
S } O }	22.0	21.84	23.50	21.87 }	1.55 20.55
	100.0	100.00	100.00	100.00	100.00

The imperfect methods of analysis used by Boussingault and Jones are sufficient explanation of the differences existing between their analyses and those of the writer.

Dumas and Cahours' methods of analysis were substantially the same as those at present in use, and their analysis is doubtless

correct, but their albumin was obtained by concentrating the solu-
tion, and it is not probable that the substance analyzed by them
was simply coagulated albumin. Ritthausen's analysis agrees well
with the writer's, except in nitrogen. He prepared coagulated
albumin, however, by acidifying his solution with nitric acid and
boiling ; therefore, differences are to be expected.

The albumin separating at 80° was present in only very small
quantity and no attempt was made to prepare it for analysis.

b.—*The Proteids remaining in Solution after Separating the Albumins.*

As already stated in describing the reaction of the extract freed
from globulin by dialysis, there was found in it one or more pro-
teoses, besides the albumins just described. These were almost
wholly precipitated by saturation with sodium chloride, or by
adding 20 per cent. of this salt to the solution together with a
little acetic acid.

If the albumins are completely removed by heat and the
filtered solution then concentrated, a coagulum gradually develops.
A similar coagulum has been found in all the extracts of seeds so
far examined by the writer. This substance must be derived from
the proteose-like proteid, as this forms nearly, if not quite all, the
proteid substance remaining in solution before concentration. If
the coagulum is removed by concentration and long-continued
heating and subsequent filtration, wholly uncoagulable proteose-
like substances are found in solution. It is nearly certain that
these are the result of alteration of the proteose first described.
The amount of proteose is extremely small and no preparations
were made for analysis. The coagula obtained by concen-
trating the solution filtered from preparations **3** and **4**, respec-
tively, were analyzed with the following result :

Coagulated Wheat Proteid, *Preparation* **6.**

	I.	II.	Average.	Ash-free.
Carbon	51.35	51.60	51.48	51.62
Hydrogen	..	..	..	..
Nitrogen	16.79	16.58	16.69	16.73
Sulphur ⎱ Oxygen ⎰	..	..	..	..
Ash	0.27	..	..	..

Ash.—0.2626 gram substance dried at 110° gave 0.0007 gram ash $=$ 0.27 per cent.

Carbon and Hydrogen, I.—0.2262 gram dried substance gave 0.4259 gram $CO_2 =$ 51.35 per cent. C, and hydrogen was lost.

II.—0.1695 gram dried substance gave 0.3207 gram $CO_2 =$ 51.60 per cent. C, and hydrogen was lost.

Nitrogen, I.—0.2510 gram dried substance gave 35.23 cc. N at 11° (barometer 756.4 mm. at 23°) $=$ 16.79 per cent.

II.—0.2873 gram dried substance gave 39.21 cc. N at 11° (barometer 768 mm. at 23°) $=$ 16.58 per cent.

Another coagulum similarly obtained from the solution filtered from preparation **4** was also analyzed and the following figures obtained :

Coagulated Wheat Proteid, *Preparation* **7.**

	I.	II.	Average.	Ash-free.
Carbon	51.73	..	51.73	51.86
Hydrogen	6.82	..	6.82	6.82
Nitrogen	17.29	17.26	17.28	17.32
Sulphur } Oxygen }	..	..	..	24.00
Ash	0.25	..	0.25	..
				100.00

Ash.—0.2820 gram substance dried at 110° gave 0.0007 gram ash $=$ 0.25 per cent.

Carbon and Hydrogen.—0.2482 gram dried substance gave 0.4708 gram $CO_2 =$ 51.73 per cent. C, and 0.1525 gram $H_2O =$ 6.82 per cent. H.

II.—0.2096 gram dried substance gave 0.3930 gram $CO_2 =$ 51.14 per cent. C, and 0.1281 gram $H_2O =$ 6.79 per cent. H.

Nitrogen, I.—0.2643 gram dried substance gave 39.21 cc. N at 17° (barometer 752.6 mm. at 22°) $=$ 17.29 per cent.

II.—0.2585 gram dried substance gave 38.02 cc. N at 17° (barometer 757.2 mm. at 20°) $=$ 17.26 per cent.

III.—Proteids Soluble in Sodium-Chloride Solution.

Beside the proteids soluble in water, 10-per cent. sodium-chloride brine extracts from ground wheat kernels a globulin which is present in the seed in small quantity. 10,000 grams of " straight flour " were extracted with 34 liters of 10-per cent. sodium-chloride solution by suspending the flour in the liquid, stirring frequently, and then allowing the whole to stand at rest over night. The extract, separated from the flour and filtered as clear as pos-

sible, had a very slight acid reaction, was of a pink color, very viscid consistence, and formed about one-half of the solution added to the flour. This was saturated with ammonium sulphate, and the resulting precipitate filtered off and dissolved as far as possible in four liters of 10-per cent. sodium-chloride brine. The exceedingly viscid solution so produced was filtered with difficulty. The clear solution, placed in a dialyzer, was left in a stream of running water until the chlorides were removed. As the salts dialyzed out, the globulin gradually separated, and under the microscope the precipitate was seen to consist of exceedingly minute particles, the larger of these being evidently spheroidal in form. This precipitate was filtered off, and, after washing with water, alcohol and ether, found to weigh, dried over sulphuric acid, 5.8 grams. This proteid, dissolved in 10-per cent. sodium-chloride solution, when heated slowly, gave a very slight turbidity at 87°, which increased slightly up to 99°. On boiling, some coagulum developed, and on adding acid to the solution filtered from this coagulum, a very considerable precipitate formed.

Dilution of the solution of the globulin in 10-per cent. sodium-chloride brine precipitated the proteid. Saturation with sodium chloride gave no precipitate. Saturation with magnesium sulphate, and also with ammonium sulphate, completely precipitated the globulin. Dried at 110° this preparation gave the following results when analyzed:

WHEAT GLOBULIN, *Preparation* 8.

	I.	II.	Average.	Ash-free.
Carbon	50.87	50.79	50.83	51.07
Hydrogen	6.74	6.67	6.71	6.75
Nitrogen	18.13	18.25	18.19	18.27
Sulphur	0.97	..	0.97	0.97
Oxygen	..	..	..	22.94
Ash	0.48	..	..	..
				100.00

Ash.—0.6010 gram substance dried at 110° gave 0.0029 gram ash = 0.48 per cent.

Carbon and Hydrogen, I.—0.2724 gram dried substance gave 0.5081 gram CO_2 = 50.87 per cent. C, and 0.1652 gram H_2O = 6.74 per cent. H.

II.—0.3169 gram dried substance gave 0.5902 gram CO_2 = 50.79 per cent. C, and 0.1905 gram H_2O = 6.67 per cent. H.

Nitrogen, I.—0.3530 gram dried substance gave 53.75 cc. N at 11° (barometer 752 mm. at 24°) = 18.13 per cent.

II.—0.2635 gram dried substance gave 39.46 cc. N at 11° (barometer 770.5 mm. at 23°) = 18.25 per cent.

Sulphur.—0.6243 gram dried substance gave 0.0441 gram $BaSO_4$ = 0.97 per cent. S.

Another preparation was made in the same way as the preceding, except the precipitation with ammonium sulphate was omitted, the filtered extract being placed at once in dialysers. Like the preceding solution, this was at first very viscid, but after the removal of the chloride the viscid property was entirely lost. This viscidity can hardly be due to the globulin, for solutions of the precipitated globulin showed no trace of it. The aqueous extract of the flour had no such property, and it is difficult to say to what this was due unless to the presence of gum. After complete removal of the chlorides the solution was filtered from the precipitate, the latter dissolved in 10-per cent. sodium-chloride solution, and the insoluble matter filtered off. The residue so removed consisted chiefly of an "albuminate" derived from the globulin. This "albuminate" was dissolved in $\frac{2}{10}$-per cent. potash solution, filtered clear, and precipitated by neutralization with $\frac{2}{10}$-per cent. hydrochloric acid. The precipitate thrown down was washed with water, alcohol and ether. Dried over sulphuric acid it weighed 2 grams. The solution of the globulin was dialyzed till free from chlorides, the separated globulin filtered off, washed with water, alcohol and ether, and after drying over sulphuric acid weighed 5 grams. The yield in this extraction was therefore 7 grams, or nearly the same as in the preceding. The composition of this preparation is given by the following analysis:

WHEAT GLOBULIN, *Preparation 9.*

	I.	II.	Average.	Ash-free.
Carbon	50.77	50.63	50.70	51.01
Hydrogen	7.03	6.84	6.93	6.97
Nitrogen	18.43	18.32	18.38	18.48
Sulphur	0.71	..	0.71	0.71
Oxygen	..	..	..	22.83
Ash	0.62	..	..	..
				100.00

Ash.—0.3685 gram substance dried at 110° gave 0.0022 gram ash = 0.62 per cent.

Carbon and Hydrogen, I.—0.2850 gram dried substance gave 0.5306 gram CO_2 = 50.77 per cent. C, and 0.1805 gram H_2O = 7.03 per cent. H.

II.—0.3700 gram dried substance gave 0.6869 gram CO_2 = 50.63 per cent. C, and 0.2278 gram H_2O = 6.84 per cent. H.

Nitrogen, I.—0.3263 gram dried substance gave 50.34 cc. N at 13° (barometer 761.2 mm. at 26°) = 18.43 per cent.

II.—0.3528 gram dried substance gave 54.16 cc. N at 13° (barometer 760.4 mm. at 28°) = 18.32 per cent.

Sulphur.—0.5190 gram dried substance gave 0.0268 gram $BaSO_4$ = 0.71 per cent. S.

The globulin contained in the "shorts" from the spring wheat was next extracted by treating 2000 grams with 10-per cent. sodium-chloride solution for three hours, with frequent stirring, and then squeezing out the extract in a screw press. After the suspended starch had settled, the extract was decanted and saturated with ammonium sulphate. The precipitate was dissolved in 10-per cent. sodium-chloride brine, and the solution filtered from the insoluble matter. The clear extract was then dialyzed till free from chlorides, and the precipitated globulin found to consist of well-formed spheroids and masses of confluent spheroids. The globulin was strongly colored, since much coloring matter was extracted from the shorts, rendering the extract a deep red-brown in color. The precipitate was then filtered off, again dissolved in the salt solution and placed in a dialyzer. When free from chlorides the precipitated globulin was filtered off and found to be still much colored. On washing with water it dissolved, and was therefore washed with dilute alcohol and ether. Dried over suphuric acid it weighed 2.22 grams, and had the following composition ·

WHEAT GLOBULIN, *Preparation* 10.

		Ash-free.
Carbon	50.79	51.00
Hydrogen	6.80	6.83
Nitrogen	18.19	18.20
Sulphur	0.66	0.66
Oxygen	. .	23.25
Ash	0.40	. .
		100.00

Ash.—0.2767 gram substance dried at 110° gave 0.0011 gram ash = 0.40 per cent.

Carbon and Hydrogen.—0.3033 gram dried substance gave 0.5649 gram CO_2 = 50.79 per cent. C, and 0.1857 gram H_2O = 6.80 per cent. H.

Nitrogen.—0.2420 gram dried substance gave 37.03 cc. N at 19° (barometer 769 mm. at 19°) = 18.19 per cent.

Sulphur.—0.5233 gram dried substance gave 0.0252 gram $BaSO_4$ = 0.66 per cent. S.

The filtrate and washings obtained from this preparation after the second precipitation by dialysis were precipitated by adding a few drops of sodium-chloride solution. The precipitate produced, which was nearly free from coloring matter, was filtered off, washed with dilute alcohol, absolute alcohol and ether, and found to weigh, when dried over sulphuric acid, 1.25 grams. When analyzed it gave the following results:

WHEAT GLOBULIN, *Preparation* 11.

		Ash-free.
Nitrogen	18.56	18.64
Ash	0.47	..

Ash.—0.5325 gram substance dried at 110° gave 0.0025 gram ash = 0.47 per cent.

Nitrogen.—0.4248 gram dried substance gave 67.60 cc. N at 19° (barometer 758 mm. at 23°) = 18.56 per cent.

The solution filtered from this preparation was next heated to boiling, and the coagulum obtained was filtered off, washed with water, alcohol, and ether and dried over sulphuric acid; this substance weighed 1.0 gram, and when analyzed it was found to contain the same amount of nitrogen as the globulin. It was considered to be a coagulated globulin. Its nitrogen content was as follows:

COAGULATED WHEAT GLOBULIN, *Preparation* 12.

	I.	II.	Average.
Nitrogen	18.15	18.43	18.29

Nitrogen, I.—0.2496 gram dried substance gave 38.52 cc. N at 16.5° (barometer 757.2 mm. at 15.5°) = 18.15 per cent. N.

II.—0.1420 gram dried substance gave 22.25 cc. N at 16° (barometer 756 mm. at 18°) = 18.43 per cent. N.

The total quantity of globulin obtained from the shorts was in this case 4.47 grams, being nearly twice as much as was similarly obtained from a like quantity of the flour.

Summary of Analyses of Wheat Globulin.

	8.	9.	10.	11.	12.	Average.
C	51.07	51.01	51.00	..	..	51.03
H	6.75	6.97	6.83	..	..	6 85
N	18.27	18.48	18.26	18.64	18.29	18.39
S }		0.71	0.66	..	..	0.69
O }	23.91	22.83	23.25	..	..	23.04
	100.00	100.00	100.00			100.00

No earlier analyses of this proteid substance are on record. Weyl[1] was the first to call attention to the presence of globulin in wheat, and says that "besides vegetable vitellin I detected in the 10-per cent. sodium-chloride extract of the pulverized seeds of wheat, peas, oats, white mustard, and sweet almonds, a second globulin substance." This he calls vegetable myosin and gives its coagulation-point as 55°–60°. It is probable that Weyl in some way mistook for a globulin the albumin already described. Later, Weyl and Bischoff[2] state, "On investigating the proteids of wheat one of us found chiefly an albuminous substance which, on account of its resemblance to myosin, was named vegetable myosin. This vegetable myosin must be the mother-substance of the gluten, since in wheat meal, together with it, other nitrogenous substances exist, at the most, only in very small amount." On what experimental evidence this statement rests the writers have been unable to discover, and in view of our experience we are at a loss to understand it.

Martin[3] considers wheat flour to contain a large amount of globulin of the myosin type, coagulating between 55°–60°, precipitated by saturation with sodium chloride and ammonium sulphate. Here again the small quantity of albumin contained in the flour has evidently been mistaken for a large quantity of vegetable myosin. This perhaps is not surprising, as the precipitates obtained by saturating sodium-chloride extracts with ammonium sulphate appear very bulky, and in the absence of an actual determination of the weight of these precipitates misleading conclusions might easily be reached. The only globulin found by the writers in extracts of wheat meal, either winter or spring wheat, is the one just described, which in properties and composition closely resembles those globulins which have been found in other seeds and assigned to the class of vegetable vitellins. The following table gives all these globulins obtained and analyzed by the writers up to the present time:

	Wheat.	Maize.	Hemp-seed.	Castor-bean.	Squash-seed.	Flax-seed.
C	51.03	51.71	51.28	51.31	51.66	51.48
H	6.85	6 85	6.84	6.97	6.89	6.94
N	18.39	18.12	18.84	18.75	18.51	18.60
S	0.69	0.86	0.87	0.76	0.88	0.81
O	23.04	22.46	22.17	22.21	22.06	22.17
	100.00	100.00	100.00	100.00	100.00	100.00

[1] Zeitschrift f. physiol. Chem. 1, p. 72.   [2] Ber. d. chem. Ges. 1880, p. 367.
[3] British Med. Jour. 2, p. 104, 1886.

IV.—Proteids Soluble in Dilute Alcohol.

As already stated, the wheat flour was found to yield to dilute alcohol a considerable amount of proteid matter. Treatment of the residue remaining after extracting the flour with 10-per cent. sodium-chloride brine likewise removed a large amount of proteid, as did also extraction of the gluten obtained by washing the dough with water. Extracts were made with alcohol under all these conditions, and the proteid extracted subjected to repeated fractional precipitations, in order to learn whether it was a single proteid body or a mixture.

a.—*Direct Extraction with Dilute Alcohol.*

5000 grams of the straight flour were extracted with 10 liters of alcohol, 0.90 specific gravity, and allowed to soak over night. The next morning the mixture was stirred, and, after settling, the clear solution poured off. Three liters more of alcohol, 0.90 sp. gr., were then added, and after standing some time the supernatant liquid was decanted. The residue was put in a screw press and squeezed nearly dry. The solution so obtained was designated "Extract 1." The residue was again treated with four liters of 0.90-sp. gr. alcohol and pressed nearly dry. This formed extract 2. The same process twice repeated gave two extracts which, when united, formed extract 3. Each of these three extracts, after filtering perfectly clear, was separately concentrated to one-third its volume, and, after cooling, decanted from the very glutinous, viscid mass which had separated. 1 and 3 yielded much more substance than 2. On stirring with a glass rod the precipitated mass formed a very thick, viscid liquid. This substance was in each case dissolved in a small amount of hot alcohol of 0.90 sp. gr., in which it was very soluble, and the solution was allowed to cool over night. Most of the substance separated on cooling and the liquid was decanted from it. The solution decanted from the second and third extracts was treated with a quantity of distilled water and a little sodium chloride added. This threw down a small precipitate, which on standing collected on the bottom of the vessel as a clear, semi-fluid mass. This was treated with water, absolute alcohol and ether, and yielded preparation **13** from extract 2, and preparation **14** from extract 3. These had the following composition :

Wheat Proteid, *Preparation* 13.

		Ash-free.
Nitrogen	17.05	17.18
Ash	0.76	

Ash.—0.7777 gram substance dried at 110° gave 0.0059 gram ash = 0.76 per cent.

Nitrogen.—0.2675 gram dried substance gave 37.22 cc. N at 6° (barometer = 760.7 mm. at 22°) = 17.05 per cent.

Wheat Proteid, *Preparation* 14.

		Ash-free.
Nitrogen	17.15	17.26
Ash	0.65	

Ash.—0.8767 gram substance dried at 110° gave 0.0057 gram ash = 0.65 per cent.

Nitrogen.—0.3556 gram dried substance gave 49.73 cc. N at 6° (barometer 761.3 mm. at 20°) = 17.15 per cent.

13 weighed 7.27 grams; **14**, 10.70 grams. On examination both were found to contain some fat which could not be wholly removed, as the substance had dried in a dense, horny form. The residues which had separated from the solutions just described were next washed by thoroughly intermixing with distilled water. The water was found to dissolve some of the proteid, which was subsequently precipitated by the addition of a little sodium-chloride solution. After standing over night this precipitate settled to the bottom of the vessel in a transparent layer, from which the solution could be completely decanted. After treating this substance with absolute alcohol it formed a voluminous, white, porous mass. This was digested for some time with ether and the substance dried over sulphuric acid. From extract 1, preparation **15** was obtained, weighing 12.4 grams; from extract 2, united with that from 3, preparation **16**, weighing 8.6 grams.

These preparations were found on analysis to have the following compositions:

Wheat Proteid, *Preparation* 15.

	I.	II.	Average.	Ash-free.
Carbon	52.40	52.58	52.49	52.52
Hydrogen	6.77	6.78	6.78	6.78
Nitrogen	17.52	17.73	17.63	17.64
Sulphur	1.05	1.11	1.08	1.08
Oxygen	..	..	..	21.98
Ash	0.06	..	..	..
				100.00

Ash.—0.5660 gram substance dried at 110° gave 0.0003 gram ash = 0.06 per cent.

Carbon and Hydrogen, I.—0.3830 gram dried substance gave 0.7359 gram $CO_2 = 52.40$ per cent. C, and 0.2334 gram $H_2O = 6.77$ per cent. H.

II.—0.3390 gram dried substance gave 0.6536 gram $CO_2 = 52.58$ per cent. C, and 0.2067 gram $H_2O = 6.78$ per cent. H.

Nitrogen, I (Kjeldahl method).—0.8799 gram dried substance gave $NH_3 = 19.7$ cc. HCl sol.(1 cc. HCl = 0.00783 gram N) = 17.52 per cent. N.

II (Dumas' method).—0.2901 gram dried substance gave 42.03 cc. N at 6° (barometer 760.1 mm. at 22°) = 17.73 per cent.

Sulphur, I.—0.5123 gram dried substance gave 0.0391 gram $BaSO_4 = 1.04$ per cent. S.

II.—0.3742 gram dried substance gave 0.0302 gram $BaSO_4 = 1.11$ per cent. S.

WHEAT PROTEID, *Preparation* 16.

		Ash-free.
Carbon	52.69	52.77
Hydrogen	6.77	6.78
Nitrogen	17.74	17.77
Sulphur	1.26	1.26
Oxygen	..	21.42
Ash	0.15	..
		100.00

Ash.—0.6659 gram substance dried at 110° gave 0.0010 gram ash = 0.15 per cent.

Carbon and Hydrogen.—0.3008 gram dried substance gave 0.5812 gram $CO_2 = 52.69$ per cent. C, and 0.1833 gram $H_2O = 6.77$ per cent. H.

Nitrogen.—0.3513 gram dried substance gave 50.34 cc. N at 6° (barometer 769 mm. at 23°) = 17.74 per cent.

Sulphur.—0.6282 gram dried substance gave 0.0577 gram $BaSO_4 = 1.26$ per cent. S.

The residues remaining after washing with distilled water were then digested with alcohol of 0.820 sp. gr., which dissolved much of the substance. After standing some time the strong alcoholic solutions were decanted from the residues and found to consist of milky liquids. The addition of a few drops of 10-per cent. sodium-chloride solution immediately produced in each a very large, curdy precipitate, the liquids from which they separated being left perfectly clear. From the solution from the first extract, which was about one liter in volume, 32.26 grams of substance were obtained, after dehydration with absolute alcohol, digestion with ether and drying over sulphuric acid. This was marked preparation **17.** From the second extract was similarly obtained preparation

18, weighing 5.34 grams, and from the third extract preparation **19**, weighing 17.43 grams. The filtrates from **17** and **18** were found to be almost wholly free from proteid, but that from **19** left on evaporation a residue which, when freed from fat, dehydrated with absolute alcohol and dried over sulphuric acid, weighed 7.53 grams, preparation **20**. These preparations were found to have the following compositions:

WHEAT PROTEID, *Preparation* 17.

		Ash-free.
Carbon	52.59	52.67
Hydrogen	6.70	6.70
Nitrogen	17.64	17.66
Sulphur	1.22	1.22
Oxygen	..	21.75
Ash	0.15	..
		100.00

Ash.—0.6727 gram substance dried at 110° gave 0.0010 gram ash = 0.15 per cent.

Carbon and Hydrogen.—0.4827 gram dried substance gave 0.9309 gram CO_2 = 52.59 per cent. C, and 0.2913 gram H_2O = 6.70 per cent. H.

Nitrogen.—0.3661 gram dried substance gave 52.85 cc. N at 7° (barometer 761.3 mm. at 20.5°) = 17.64 per cent.

Sulphur.—0.7524 gram dried substance gave 0.0667 gram $BaSO_4$ = 1.22 per cent. S.

WHEAT PROTEID, *Preparation* 18.

	I.	II.	Average.	Ash-free.
Carbon	52.28	52.54	52.41	52.55
Hydrogen	6.87	6.79	6.83	6.85
Nitrogen	17.90	..	17.90	17.94
Sulphur	1.21	..	1.21	1.21
Oxygen	..	..	..	21.45
Ash	0.27	..	..	..
				100.00

Ash.—0.7722 gram substance dried at 110° gave 0.0021 gram ash = 0.27 per cent.

Carbon and Hydrogen, I.—0.3534 gram dried substance gave 0.6774 gram CO_2 = 52.28 per cent. C, and 0.2187 gram H_2O = 6.87 per cent. H.

II.—0.3290 gram dried substance gave 0.6338 gram CO_2 = 52.54 per cent. C, and 0.2010 gram H_2O = 6.79 per cent. H.

Nitrogen.—0.3922 gram dried substance gave 57.73 cc. N at 7° (barometer 758 mm. at 22°) = 17.90 per cent.

Sulphur.—0.7080 gram dried substance gave 0.0625 gram $BaSO_4$ = 1.21 per cent. S.

WHEAT PROTEID, *Preparation* 19.

	I.	II.	Average.	Ash-free.
Carbon	52.52	52.82	52.67	52.74
Hydrogen	6.72	6.79	6.76	6.77
Nitrogen	17.60	..	17.60	17.62
Sulphur	1.23	..	1.23	1.23
Oxygen	..	..	..	21.64
Ash	0.14	..	..	..
				100.00

Ash.—0.5696 gram substance dried at 110° gave 0.0008 gram ash = 0.14 per cent.

Carbon and Hydrogen, I.—0.3338 gram dried substance gave 0.6429 gram CO_2 = 52.52 per cent. C, and 0.2020 gram H_2O = 6.72 per cent. H.

II.—0.3135 gram dried substance gave 0.6072 gram CO_2 = 52.82 per cent. C, and 0.1916 gram H_2O = 6.79 per cent. H.

Nitrogen.—0.2980 gram dried substance gave 43.24 cc. N at 5° (barometer 750.7 mm. at 23°) = 17.60 per cent.

Sulphur.—0.7703 gram dried substance gave 0.0687 gram $BaSO_4$ = 1.23 per cent. S.

WHEAT PROTEID, *Preparation* 20.

	I.	II.	Average.	Ash-free.
Carbon	52.13	52.42	52.28	52.39
Hydrogen	6.97	6.85	6.91	6.93
Nitrogen	17.35	17.19	17.27	17.31
Sulphur	1.35	1.41	1.38	1.38
Oxygen	..	..	..	21.99
Ash	0.22	..	..	..
				100.00

Ash.—0.7550 gram substance dried at 110° gave 0.0017 gram ash = 0.22 per cent.

Carbon and Hydrogen, I.—0.3235 gram dried substance gave 0.6184 gram CO_2 = 52.13 per cent. C, and 0.2030 gram H_2O = 6.97 per cent. H.

II.—0.3679 gram dried substance gave 0.7072 gram CO_2 = 52.42 per cent. C, and 0.2265 gram H_2O = 6.85 per cent. H.

Nitrogen, I.—0.2916 gram dried substance gave 41.42 cc. N at 6° (barometer 757 mm. at 22°) = 17.35 per cent.

II.—0.2703 gram dried substance gave 37.82 cc. N at 6° (barometer 761.3 mm. at 21°) = 17.19 per cent.

Sulphur, I.—0.6960 gram dried substance gave 0.0683 gram $BaSO_4$ = 1.35 per cent. S.

II.—0.6389 gram dried substance gave 0.0655 gram $BaSO_4$ = 1.41 per cent. S.

The residues which remained after treatment with alcohol of 0.820 sp. gr. were then dehydrated with absolute alcohol and digested with ether. After drying over sulphuric acid there was obtained from extract 1, preparation **21**, weighing 63.0 grams; from extract 2, preparation **22**, weighing 2.1 grams; and from extract 3, preparation **23**, weighing 41.2 grams.

WHEAT PROTEID, *Preparation* **21**.

		Ash-free.
Carbon	52.81	52.84
Hydrogen	6.81	6.81
Nitrogen	17.66	17.67
Sulphur	1.11	1.11
Oxygen	..	21.57
Ash	0.06	..
		100.00

Ash.—1.1986 grams substance dried at 110° gave 0.0008 gram ash = 0.06 per cent.

Carbon and Hydrogen.—0.3686 gram dried substance gave 0.7138 gram $CO_2 = 52.81$ per cent. C, and 0.2260 gram $H_2O = 6.81$ per cent. H.

Nitrogen.—0.4639 gram dried substance gave 67 cc. N at 7° (barometer 762 mm. at 21°) = 17.66 per cent.

Sulphur.—0.7527 gram dried substance gave 0.0610 gram $BaSO_4 = 1.11$ per cent. S.

WHEAT PROTEID, *Preparation* **22**.

	I.	II.	Average.	Ash-free.
Nitrogen	15.42	15.28	15.35	15.42
Ash	0.42	..	0.42	..

Ash.—0.6362 gram substance dried at 110° gave 0.0027 gram ash = 0.42 per cent.

Nitrogen, I (Kjeldahl method).—0.5380 gram dried substance gave $NH_3 = 10.6$ cc. HCl sol. (1 cc. = 0.00783 gram N) = 15.42 per cent. N.

Nitrogen, II (Dumas' method).—0.3114 gram dried substance gave 39.21 cc. N at 12° (barometer 769.6 mm. at 21.5°) = 15.28 per cent.

WHEAT PROTEID, *Preparation* **23**.

	I.	II.	Average.	Ash-free.
Carbon	52.90	52.99	52.95	53.02
Hydrogen	6.74	6.82	6.78	6.79
Nitrogen	17.24	17.36	17.30	17.32
Sulphur	1.05	..	1.05	1.05
Oxygen	..	..	..	21.82
Ash	0.15	..	..	..
				100.00

Ash.—0.7720 gram substance dried at 110° gave 0.0012 gram ash = 0.15 per cent.

Carbon and Hydrogen, I.—0.3829 gram dried substance gave 0.7427 gram $CO_2 = 52.90$ per cent. C, and 0.2325 gram $H_2O = 6.74$ per cent. H.

II.—0.3433 gram dried substance gave 0.6671 gram $CO_2 = 52.99$ per cent. C, and 0.2108 gram $H_2O = 6.82$ per cent. H.

Nitrogen, I (Kjeldahl method).—0.5676 gram dried substance gave $NH_3 = 12.5$ cc. HCl sol. (1 cc. HCl = 0.00783 gram N) = 17.24 per cent. N.

II (Dumas' method).—0.3571 gram dried substance gave 51.54 cc. N at 6° (barometer 747 mm. at 22°) = 17.36 per cent.

Sulphur.—0.5733 gram dried substance gave 0.0441 gram $BaSO_4 = 1.05$ per cent. S.

Preparation **21**, which constituted the principal fraction of the proteid extracted, was further treated in the following manner : Twenty grams were dissolved in 250 cc. of 0.90-sp. gr. alcohol and found to yield a clear solution, which was then poured into 800 cc. of absolute alcohol, whereby a considerable precipitate was at once separated, leaving the solution milky. This substance was dehydrated with absolute alcohol and digested with ether, yielding preparation **24**. The filtrate was then treated with a few drops of 10·per cent. sodium-chloride solution, causing a heavy precipitate, which on stirring rapidly agglutinated and adhered as a mass to the stirring-rod. This was removed, treated in the usual manner, and marked preparation **25**. The mother-liquor from which this separated, after standing over night, deposited a further small amount of proteid, which, after treatment with absolute alcohol and ether, gave preparation **26**. These three substances were analyzed and found to have the following compositions :

WHEAT PROTEID, *Preparation* **24**.

		Ash-free.
Nitrogen	17.67	17.69
Ash	0.10	..

Ash.—0.6064 gram substance dried at 110° gave 0.0006 gram ash = 0.10 per cent.

Nitrogen.—0.4073 gram dried substance gave 61.10 cc. N at 16° (barometer 756.6 mm. at 15°) = 17.67 per cent.

WHEAT PROTEID, *Preparation* **25**.

	I.	II.	Average.	Ash-free.
Carbon	52.15	52.35	52.25	52.33
Hydrogen	6.93	6.87	6.90	6.91
Nitrogen	17.52	17.84	17.68	17.70
Sulphur ⎫ Oxygen ⎬	..	..	..	23.06
Ash	0.15	..	..	..
				100.00

Ash.—0.6683 gram substance dried at 110° gave 0.0010 gram ash $=$ 0.15 per cent.

Carbon and Hydrogen, I.—0.3842 gram dried substance gave 0.7347 gram $CO_2 = 52.15$ per cent. C, and 0.2398 per cent. $H_2O = 6.93$ per cent. H.

II.—0.3291 gram dried substance gave 0.6316 gram $CO_2 = 52.35$ per cent. C, and 0.2035 gram $H_2O = 6.87$ per cent. H.

Nitrogen, I.—0.4639 gram dried substance gave 69.2 cc. N at 16.5° (barometer 756 mm. at 18°) $=$ 17.52 per cent.

II.—0.4538 gram dried substance gave 69.6 cc. N at 17° (barometer 750 mm. at 18°) $=$ 17.84 per cent.

WHEAT PROTEID, *Preparation* 26.

		Ash-free.
Carbon	52.28	52.38
Hydrogen	7.12	7.13
Nitrogen	17.79	17.82
Sulphur ⎱ Oxygen ⎰	..	22.67
Ash	0.19	..
		100.00

Ash.—0.6300 gram substance dried at 110° gave 0.0012 gram ash $=$ 0.19 per cent.

Carbon and Hydrogen.—0.3162 gram dried substance gave 0.6061 gram $CO_2 = 52.28$ per cent. C, and 0.2027 gram $H_2O = 7.12$ per cent. H.

Nitrogen.—0.3932 gram dried substance gave 60.32 cc. N at 17° (barometer 748.2 mm. at 19°) $=$ 17.79 per cent. N.

If the preceding analyses are brought together as in the following table, the effect of the various fractional solutions and precipitations may be seen at a glance.

Proteid extracted by Direct Treatment of the Flour with Alcohol.

	From 0.9 sp. gr. Alcoholic Solution.		From Water Washings.	
	13.	14.	15.	16.
Carbon	..	..	52.52	52.77
Hydrogen	..	..	6.78	6.78
Nitrogen	17.18	17.26	17.64	17.77
Sulphur	..	..	1.08	1.26
Oxygen	..	..	21.98	21.42
			100.00	100.00
Weight of substance in grams ⎰	7.27	10.70	12.40	8.60

	From 0 82 Alcoholic Solution.			From Filtrate from **19**.
	17.	18.	19.	20.
Carbon	52.67	52.55	52.74	52.39
Hydrogen	6.70	6.85	6.77	6.93
Nitrogen	17.66	17.94	17.62	17.31
Sulphur	1.22	1.21	1.23	1.38
Oxygen	21.75	21.45	21.64	21.99
	100.00	100.00	100.00	100.00
Weight of substance in grams	32.26	5.34	17.43	7.53

	Residue after Extraction with 0.820 Alcohol.			Fractional Reprecipitations of Preparation **21**.		
	21.	22.	23.	24.	25.	26.
Carbon	52.82	..	53.02	..	52.33	52.38
Hydrogen	6 81	..	6.79	..	6.91	7.13
Nitrogen	17.67	15.42	17.32	17.69	17.70	17.82
Sulphur	1.11	..	1.05	.. }	23.06	22.67
Oxygen	21.57	..	21.82	.. }		
	100.00		100.00		100.00	100.00
Weight of substance in grams	63.0	2.10	41.20	..	..	..

It is evident that **13** and **14** contain less nitrogen than the great bulk of the proteid extracted. This is due to fat which they were found to contain and which could not be wholly removed by extraction with ether, since in drying these preparations were converted into the horny condition which rendered penetration with ether impossible. By grinding fine and extracting with ether some fat was removed, which proved the correctness of this supposition.

22 was evidently impure, as might be expected, since it contained all of the insoluble particles of the entire extract which had escaped filtration, and owing to its small amount these impurities produced a marked effect on its percentage composition. The same is true of **23**, but as the quantity of proteid is so much greater, this contamination has produced much less effect on its composition. **20** was obtained by evaporating the mother-liquor from **19** nearly to dryness and then extracting with absolute alcohol and ether. It would hardly be expected that under such circumstances it would be absolutely pure. The other preparations are in remarkable agreement, and it is evident that no fractional separation of the extracted proteid has been effected. The

preparations obtained from solution in pure water have the same composition as those from solutions in alcohol of 0.820 sp. gr., and also the same composition as the residue remaining after treatment with each of these reagents. It may safely be concluded that the wheat contains but one proteid soluble in dilute alcohol, especially when the experiments next to be described are considered.

The total amount of proteid contained in these several preparations is 207.83 grams, being equal to 4.16 per cent. of the flour.

b.—Extraction with Dilute Alcohol after extracting the Flour with 10-per cent. Sodium-Chloride Solution.

4000 grams of "straight flour" were extracted with 10-per cent. sodium-chloride brine as long as anything was removed. After squeezing as dry as possible in a screw press, the residue was treated with alcohol so as to yield with the water retained by the meal as nearly as possible a solution containing 75 per cent. of alcohol. After digesting two days with the solvent, the extract was squeezed out in a press and the process repeated three times. Four extracts were thus obtained. These were each concentrated to small volume, cooled, and the solution decanted from the precipitated mass. This was then washed with distilled water. After removing the salts the substance from extracts 1 and 2 dissolved to some extent; that from extract 3 dissolved completely to a turbid solution. By adding sodium chloride the dissolved proteid was precipitated completely.

The residues remaining after washing with water were treated with absolute alcohol, digested with ether and dried over sulphuric acid. The precipitates obtained from the water washings by adding salt were treated in the same way. From extract 1, preparation **27** was obtained, weighing 82.0 grams; from extract 2, preparation **28**, weighing 57.0 grams; from extract 3, after dissolving in water and precipitating with sodium chloride, preparation **29**, weighing 11.3 grams; from extract 4, preparation **30**, weighing only 1.35 grams; and from the united water washings of **27** and **28**, preparation **31**, weighing 5.8 grams. The total weight of these preparations was 157.45 grams, equal to 3.94 per cent. of the flour taken. Their composition is shown by the following analyses.

WHEAT PROTEID, *Preparation* 27.

	I.	II.	Average.	Ash-free.
Carbon	52.61	..	52.61	52.69
Hydrogen	6.82	..	6.82	6.84
Nitrogen	17.62	17.78	17.70	17.73
Sulphur	1.00	1.04	1.02	1.02
Oxygen	..	..	..	21.72
Ash	0.16	..	..	..
				100.00

Ash.—0.6194 gram substance dried at 110° gave 0.0010 gram ash = 0.16 per cent.

Carbon and Hydrogen.—0.3678 gram dried substance gave 0.7095 gram CO_2 = 52.61 per cent. C, and 0.2259 gram H_2O = 6.82 per cent. H.

Nitrogen, I (Kjeldahl method).—0.8977 gram dried substance gave NH_3 = 20.2 cc. HCl sol. (1 cc. HCl sol. = 0.00783 gram N) = 17.62 per cent. N.

II (Dumas' method).—0.3396 gram dried substance gave 48.72 cc. N at 6° (barometer 769.3 mm. at 21°) = 17.78 per cent.

Sulphur, I.—0.6734 gram dried substance gave 0.0491 gram $BaSO_4$ = 1.00 per cent. S.

II.—0.5685 gram dried substance gave 0.0431 gram $BaSO_4$ = 1.04 per cent. S.

WHEAT PROTEID, *Preparation* 28.

	I.	II.	Average.	Ash-free.
Carbon	52.65	..	52.65	52.72
Hydrogen	6.85	..	6.85	6.86
Nitrogen	17.87	..	17.87	17.89
Sulphur	0.95	0.94	0.95	0.95
Oxygen	..	..	..	21.58
Ash	0.13	..	..	..
				100.00

Ash.—0.6194 gram substance dried at 110° gave 0.0010 gram ash = 0.16 per cent.

Carbon and Hydrogen.—0.3730 gram dried substance gave 0.7202 gram CO_2 = 52.65 per cent. C, and 0.2301 gram H_2O = 6.85 per cent. H.

Nitrogen.—0.2863 gram dried substance gave 41.83 cc. N at 6° (barometer 759.6 mm. at 21°) = 17.87 per cent.

Sulphur, I.—0 6916 gram dried substance gave 0.0480 gram $BaSO_4$ = 0.95 per cent. S.

II.—0.7947 gram dried substance gave 0.0545 gram $BaSO_4$ = 0.94 per cent. S.

WHEAT PROTEID, *Preparation* 29.

	I.	II.	Average.	Ash-free.
Carbon	52.52	52.67	52.60	52.71
Hydrogen	6.82	6.76	6.79	6.81
Nitrogen	17.72	..	17.72	17.75
Sulphur	1.10	..	1.10	1.10
Oxygen	..	..	..	21 63
Ash	0.21	..	..	..
				100.00

Ash.—0.4231 gram substance dried at 110° gave 0.0009 gram ash $=$ 0.21 per cent.

Carbon and Hydrogen, I.—0.3075 gram dried substance gave 0.5922 gram $CO_2 = 52.52$ per cent. C, and 0.1887 gram $H_2O = 6.82$ per cent. H.

II.—0.3338 gram dried substance gave 0.6447 gram $CO_2 = 52.67$ per cent. C, and 0.2030 gram $H_2O = 6.76$ per cent. H.

Nitrogen.—0.3296 gram dried substance gave 48.04 cc. N at 14° (barometer 755.2 mm. at 22°) $=$ 17.72 per cent.

Sulphur.—0.7409 gram dried substance gave 0.0596 gram $BaSO_4 = 1.10$ per cent. S.

WHEAT PROTEID, *Preparation* 30.

		Ash-free.
Nitrogen	16.93	17.08
Ash	0.91	..

Ash.—0.3075 gram substance dried at 110° gave 0.0028 gram ash $=$ 0.91 per cent.

Nitrogen (Kjeldahl method).—0.7401 gram dried substance gave $NH_3 =$ 16 cc. HCl sol. (1 cc. HCl sol. $=$ 0.00783 gram N) $=$ 16.93 per cent. N.

WHEAT PROTEID, *Preparation* 31.

		Ash-free.
Carbon	52.62	52.65
Hydrogen	6.83	6.83
Nitrogen	17.78	17.79
Sulphur	1.08	1.08
Oxygen	..	21.65
Ash	0.05	..
	100.00	

Ash.—0.7826 gram substance dried at 110° gave 0.0004 gram ash $=$ 0.05 per cent.

Carbon and Hydrogen.—0.3081 gram dried substance gave 0.5945 gram $CO_2 = 52.62$ per cent. C, and 0.1896 gram $H_2O = 6.83$ per cent. H.

Nitrogen.—0.3084 gram dried substance gave 45.04 cc. N at 6° (barometer 755.5 mm. at 20.5°) $=$ 17.78 per cent. N.

Sulphur.—0.6815 gram dried substance gave 0.0539 gram $BaSO_4 = 1.08$ per cent. S.

c.—Extraction of Gluten with Dilute Alcohol.

2000 grams of "straight spring wheat flour" were made into a dough with distilled water of 20°, and then washed in a stream of river water of 5°. After washing until nearly all the starch was removed, the gluten was chopped up fine and digested with alcohol of 0.90 sp. gr., at a temperature of about 20°. This extraction was continued with repeatedly renewed portions of alcohol of the same strength, as long as anything was removed. The extracts were united, filtered perfectly clear, and concentrated to about one-fourth their original volume. The residual solution was then cooled and allowed to stand over night to deposit the separated proteid. The supernatant solution was poured off, and the large amount of proteid which had separated was then dehydrated by treatment with absolute alcohol. The decanted mother-liquor from which this proteid had separated, and also the strong alcoholic solution which resulted from dehydrating the precipitated mass, were each precipitated by adding a little sodium-chloride solution. The three products thus obtained were united, digested with fresh quantities of absolute alcohol, in order to complete the dehydration, and then extracted with absolute ether. Dried over sulphuric acid the preparation weighed 82.0 grams, and formed therefore 4.10 per cent. of the flour taken. Dried at 110° this substance had the following composition:

WHEAT PROTEID, *Preparation* 32.

		Ash-free.
Carbon	52.33	52.58
Hydrogen	6.63	6.67
Nitrogen	17.57	17.65
Sulphur	1.08	1.08
Oxygen	..	22.02
Ash	0.50	..
		100.00

Ash.—0.4222 gram substance dried at 110° gave 0.0021 gram ash = 0.50 per cent.

Carbon and Hydrogen.—0.3697 gram dried substance gave 0.7094 gram CO_2 = 52.33 per cent. C, and 0.2207 gram H_2O = 6.63 per cent. H.

Nitrogen.—0.3193 gram dried substance gave 46.47 cc. N at 11° (barometer 763 mm. at 23°) = 17.57 per cent.

Sulphur.—0.4734 gram dried substance gave 0.0372 gram $BaSO_4$ = 1.08 per cent. S.

Thirty grams of preparation **32** were then dissolved in alcohol of 0.90 sp. gr., and the clear solution evaporated to small volume, cooled, and as no proteid separated, strong alcohol was added until a considerable precipitate resulted, equal to about one-half the dissolved proteid. This precipitate which, if the extracted proteid were a mixture, as stated by Ritthausen, would contain the bulk of the substances insoluble in strong alcohol, was then dehydrated by absolute alcohol and dried over sulphuric acid. It was found to weigh 12 grams. This was marked preparation **33**.

The solution from which this substance had separated must have contained the chief part of the proteid called by Ritthausen gluten fibrin. It was then concentrated to small volume, cooled, water added until a considerable precipitate resulted, the solution then heated until all dissolved, and, after cooling, the mother-liquor was decanted from the separated proteid. This process was repeated four times, and the precipitate finally obtained dehydrated with absolute alcohol, digested with ether, and dried over sulphuric acid. This preparation, **34**, weighed 1.6 grams.

WHEAT PROTEID, *Preparation* **33**.

		Ash-free.
Carbon	52.58	52.68
Hydrogen	6.77	6.78
Nitrogen	17.62	17.65
Sulphur	1.09	1.09
Oxygen	..	21.80
Ash	0.19	..
		100.00

Ash.—0.5204 gram substance dried at 110° gave 0.0010 gram ash $=$ 0.19 per cent.

Carbon and Hydrogen.—0.3339 gram dried substance gave 0.6438 gram CO_2 $=$ 52.58 per cent. C, and 0.2035 gram H_2O $=$ 6.77 per cent. H.

Nitrogen.—0.3509 gram dried substance gave 51.74 cc. N at 11° (barometer 755.6 mm. at 22°) $=$ 17.62 per cent. N.

Sulphur.—0.6358 gram dried substance gave 0.0506 gram $BaSO_4$ $=$ 1.09 per cent. S.

WHEAT PROTEID, *Preparation* **34**.

		Ash-free.
Carbon	52.82	52.84
Hydrogen	7.18	7.18
Nitrogen	17.57	17.57
Sulphur } Oxygen	..	22.41
Ash	0.04	..
		100.00

Ash.—0.4995 gram substance dried at 110° gave 0.0002 gram ash = 0.04 per cent.

Carbon and Hydrogen.—0.1807 gram dried substance gave 0.3500 gram CO_2 = 52.82 per cent. C, and 0.1168 gram H_2O = 7.18 per cent. H.

Nitrogen.—0.3592 gram dried substance gave 52.25 cc. N at 11° (barometer 763.7 mm. at 25°) = 17.57 per cent.

It is clear from these analyses that no separation into proteids of differing composition had thus been effected.

d.—*Extraction of "Shorts" with Dilute Alcohol.*

2000 grams of "shorts" from the spring wheat flour were extracted with alcohol of 0.90 sp. gr., and the extract squeezed out with a screw press. The extract, which was a deep red-brown in color, was filtered perfectly clear, and then concentrated by distillation to about one-third. On cooling the proteid separated, leaving the mother-liquor as a deep coffee-brown liquid. This was decanted, the precipitate dissolved in alcohol of 0.90 sp. gr., and again precipitated by concentration and cooling, the strongly colored mother-liquor was decanted and this process repeated. The precipitated proteid was then again dissolved in a little dilute alcohol, and the resulting solution poured into absolute alcohol, thereby precipitating the greater part of the proteid and leaving the alcohol strongly colored. The precipitate was thus freed from a very considerable part of its coloring matter. After digestion with absolute alcohol, and finally with ether, it was dried and analyzed with the following result:

WHEAT PROTEID, *Preparation* 35.

		Ash-free.
Carbon	52.75	53.25
Hydrogen	6.96	7.02
Nitrogen	17.22	17.38
Sulphur	1.36	1.37
Oxygen	..	20.98
Ash	0.95	..
		100.00

Ash.—0.4210 gram substance dried at 110° gave 0.0040 gram ash = 0.95 per cent.

Carbon and Hydrogen.—0.3260 gram dried substance gave 0.6306 gram CO_2 = 52.75 per cent. C, and 0.2043 gram H_2O = 6.96 per cent. H.

Nitrogen.—0.2693 gram dried substance gave 39.21 cc. N at 19° (barometer 768.5 mm. at 21°) $=$ 17.22 per cent.

Sulphur.—0.4224 gram dried substance gave 0.0420 gram $BaSO_4 =$ 1.36 per cent. S.

Owing to the fact that this preparation was still contaminated with coloring matter, and also showed slight differences in composition from the proteid extracted by similar treatment from the flour, it was subjected to further treatment with a view to its more complete purification.

A part of the preparation was dissolved in 150 cc. of alcohol of 0.90 sp. gr. and poured into 1000 cc. of absolute alcohol. This produced a turbid liquid, which, on adding a drop or two of sodium-chloride solution, gave a heavy precipitate that rapidly settled, leaving the alcohol colored yellow. This precipitate was again dissolved in diluted alcohol, and precipitated by pouring into ether in order to remove anything soluble in this liquid. No coloring matter was thus removed. The precipitate was then digested with absolute alcohol and dried over sulphuric acid, yielding preparation 36.

The strong alcoholic solution from which this preparation had separated, on longer standing deposited a small amount of substance which, when dehydrated, yielded preparation 37. Analysis showed these two substances to have the following composition:

WHEAT PROTEID, *Preparation* 36.

	I.	II.	Average.	Ash-free.
Carbon	52.57	52.52	52.55	52.85
Hydrogen	6.74	6.80	6.77	6.81
Nitrogen	17.39	..	17.39	17.48
Sulphur) Oxygen)	..	..	..	22.86
Ash	0.54	..	..	..
				100.00

Ash.—0.5215 gram substance dried at 110° gave 0.0028 gram ash $=$ 0.54 per cent.

Carbon and Hydrogen, I.—0.3176 gram dried substance gave 0.6122 gram $CO_2 =$ 52.57 per cent. C, and 0.1924 gram $H_2O =$ 6.74 per cent. H.

II.—0.3263 gram dried substance gave 0.6283 gram $CO_2 =$ 52.52 per cent. C, and 0.1990 gram $H_2O =$ 6.80 per cent. H.

Nitrogen.—0.4450 gram dried substance gave 66.68 cc. N at 17° (barometer 748.5 mm. at 18.5°) $=$ 17.39 per cent. N.

WHEAT PROTEID, *Preparation* 37.

	I.	II.	Average.	Ash-free.
Carbon	52.43	52.56	52.50	52.74
Hydrogen	6.79	6.88	6.84	6.87
Nitrogen	17.59	..	17.59	17.67
Sulphur } Oxygen }	..	..	..	22.72
Ash	0.46	..	..	..
				100.00

Ash.—0.3467 gram substance dried at 110° gave 0.0016 gram ash = 0.46 per cent.

Carbon and Hydrogen, I.—0.3292 gram dried substance gave 0.6329 gram CO_2 = 52.43 per cent. C, and 0.2013 gram H_2O = 6.79 per cent. H.

II.—0.3159 gram dried substance gave 0.6062 gram CO_2 = 52.56 per cent. C, and 0.1958 gram H_2O = 6.88 per cent. H.

Nitrogen.—0.3426 gram dried substance gave 51.64 cc. N at 16.5° (barometer 751.6 mm. at 18.5°) = 17.59 per cent. N.

These figures show that the proteid extracted from the bran has the same composition as that similarly obtained from the flour.

e.—Proteid extracted by Alcohol from whole Wheat Flour.

As Ritthausen and probably others used whole wheat flour in extracting the various proteids described by them as soluble in dilute alcohol, it was thought best to carry out some extractions with meal obtained by grinding the entire wheat kernel in the laboratory.

1000 grams of whole spring wheat flour, freshly ground, were made into a dough, and the gluten obtained from this by washing with water. The resulting gluten was then chopped fine and thoroughly extracted with alcohol of 0.90 sp. gr., the yellow extract concentrated and the proteid separated by cooling. The deposit thus produced was dissolved as far as possible in dilute alcohol, and the insoluble substance, which was coagulated proteid, was washed with dilute alcohol, absolute alcohol and ether, and dried over sulphuric acid. This was preparation 38.

The solution filtered from 38 was poured into absolute alcohol and a small amount of proteid separated; this was treated with absolute alcohol and ether in the usual way, yielding preparation 39. The filtrate from 39 was concentrated to small volume and poured into absolute alcohol, whereby nearly all the proteid was

precipitated. This substance was dehydrated with absolute alcohol and digested with ether, giving preparation **40**. These three bodies had the composition shown by the following figures:

COAGULATED WHEAT PROTEID, *Preparation* **38**.

	I.	II.	Average.	Ash-free.
Carbon	52.88	52.68	52.78	52.90
Hydrogen	7.00	6.97	6.98	6.99
Nitrogen	17.47	17.48	17.48	17.52
Sulphur	1.43	..	1.43	1.43
Oxygen	..	..	..	21.16
Ash	0.23	..	..	..
				100.00

Ash.—0.4323 gram substance dried at 110° gave 0.0010 gram ash = 0.23 per cent.

Carbon and Hydrogen, I.—0.2522 gram dried substance gave 0.4890 gram CO_2 = 52.88 per cent. C, and 0.1587 gram H_2O = 7.00 per cent. H.

II.—0.2802 gram dried substance gave 0.5413 gram CO_2 = 52.68 per cent. C, and 0.1760 gram H_2O = 6.97 per cent. H.

Nitrogen, I.—0.2985 gram dried substance gave 44.24 cc. N at 16° (barometer 757.3 mm. at 17°) = 17.47 per cent.

II.—0.3305 gram dried substance gave 49.33 cc. N at 19° (barometer 760.7 mm. at 20°) = 17.48 per cent.

Sulphur.—0.3560 gram dried substance gave 0.0371 gram $BaSO_4$ = 1.43 per cent. S.

WHEAT PROTEID, *Preparation* **39**.

	I.	II.	Average.	Ash-free.
Carbon	52.59	52.73	52.66	52.89
Hydrogen	6.87	6.80	6.84	6.87
Nitrogen	17.92	18.06	17.99	18.06
Sulphur	0.92	..	0.92	0.92 .
Oxygen	..	..	..	21.26
Ash	0.45	..	..	..
				100.00

Ash.—0.4190 gram dried substance gave 0.0019 gram ash = 0.45 per cent.

Carbon and Hydrogen, I.—0.3267 gram dried substance gave 0.6300 gram CO_2 = 52.59 per cent. C, and 0.2022 gram H_2O = 6.87 per cent. H.

II.—0.2975 gram dried substance gave 0.5752 gram CO_2 = 52.73 per cent. C, and 0.1820 gram H_2O = 6.80 per cent. H.

Nitrogen, I.—0.3637 gram dried substance gave 56.15 cc. N at 20° (barometer 757.2 mm. at 24°) = 17.92 per cent.

II.—0.4018 gram dried substance gave 61.89 cc. N at 20° (barometer 764.8 mm. at 25°) = 18.06 per cent.

Sulphur.—0.4711 gram dried substance gave 0.0316 gram $BaSO_4$ = 0.92 per cent. S.

Wheat Proteid, *Preparation* 40.

	I.	II.	Average.	Ash-free.
Carbon	51.03	50.93	50.98	53.16
Hydrogen	6.59	6.50	6.55	6.83
Nitrogen	16.98	17.08	17.03	17.75
Sulphur	0.92	..	0.92	0.96
Oxygen	..	..	..	21.30
Ash	4.11	4.03	4.07	..
				100.00

Ash, I.—0.5397 gram substance dried at 110° gave 0.0222 gram ash = 4.11 per cent.

II.—0.4313 gram dried substance gave 0.0174 gram ash = 4.03 per cent.

Carbon and Hydrogen, I.—0.2652 gram dried substance gave 0.4962 gram $CO_2 = 51.03$ per cent. C, and 0.1574 gram $H_2O = 6.59$ per cent. H.

II.—0.3378 gram dried substance gave 0.6308 gram $CO_2 = 50.93$ per cent. C, and 0.1976 gram $H_2O = 6.50$ per cent. H.

Nitrogen, I.—0.3518 gram dried substance gave 51.34 cc. N at 20° (barometer 758.7 mm. at 22°) = 16.98 per cent.

II.—0.3100 gram dried substance gave 45.23 cc. N at 19° (barometer 761 mm. at 21°) = 17.08 per cent.

Sulphur.—0.3458 gram dried substance gave 0.0233 $BaSO_4 = 0.92$ per cent. S.

In a similar manner an extract was made of winter wheat meal, obtained by grinding the entire wheat kernel in the laboratory, the alcoholic extract cencentrated to about one-third its volume, cooled, and the solution decanted from the deposited proteid. This was then dissolved in alcohol of 0.90 sp. gr. and the coagulated proteid filtered off, washed with dilute alcohol, digested with absolute alcohol and then with ether, giving preparation **41**. The solution filtered from this preparation was concentrated to small volume, cooled, and the proteid which separated was digested with absolute alcohol and with ether, yielding preparation **42**.

Coagulated Wheat Proteid, *Preparation* 41.

		Ash-free.
Carbon	52.64	52.82
Hydrogen	6.86	6.88
Nitrogen	17.49	17.55
Sulphur ⎱ Oxygen ⎰	..	22.75
Ash	0.35	..
		100.00

Ash.—0.4275 gram substance dried at 110° gave 0.0015 gram ash = 0.35 per cent.

Carbon and Hydrogen.—0.3232 gram dried substance gave 0.1995 gram $H_2O = 6.86$ per cent. H, and 0.6234 gram $CO_2 = 52.64$ per cent. C.

Nitrogen.—0.3316 gram dried substance gave 48.51 cc. N at 11° (barometer 754.8 mm. at 18°) = 17.49 per cent.

WHEAT PROTEID, *Preparation* 42.

		Ash-free.
Carbon	52.66	52.68
Hydrogen	6.80	6.81
Nitrogen	17.62	17.63
Sulphur } Oxygen }	..	22.88
Ash	0.04	..
		100.00

Ash.—0.4731 gram substance dried at 110° gave 0.0002 gram ash = 0.04 per cent.

Carbon and Hydrogen.—0.2769 gram dried substance gave 0.5347 gram $CO_2 = 52.66$ per cent. C, and 0.1686 gram $H_2O = 6.80$ per cent. H.

Nitrogen.—0.3575 gram dried substance gave 52.17 cc. N at 10° (barometer 760.1 mm. at 22°) = 17.62 per cent.

The complete extraction of this proteid from the gluten is very difficult, a little generally remaining in the insoluble residue after extracting with dilute alcohol.

In one case the residue thus remaining was dissolved in $\frac{2}{10}$-per cent. potash water, and the resulting solution, after standing some time to deposit suspended impurities, was decanted and precipitated with dilute hydrochloric acid. This precipitate was washed by decantation with water and then digested for some time with dilute alcohol. The alcoholic solution was then filtered and concentrated to small volume and cooled. The proteid separated was then digested with absolute alcohol and with ether, and dried at 110° for analysis. From this analysis it is seen that the proteid soluble in dilute alcohol is not changed in composition by solution in potash water, nor is its solubility altered so far as could be learned.

WHEAT PROTEID, *Preparation* 43.

	I.	II.	Average.	Ash-free.
Carbon	52.03	51.88	51.96	52.24
Hydrogen	6.66	6.69	6.68	6.71
Nitrogen	17.48	..	17.48	17.57
Sulphur	1.08	..	1.08	1.08
Oxygen	..	..	..	22.40
Ash	0.52	..	..	..
				100.00

Ash.—0.4222 gram substance dried at 110° gave 0.0022 gram ash = 0.52 per cent.

Carbon and Hydrogen, I.—0.2763 gram dried substance gave 0.5271 gram CO_2 = 52.03 per cent. C, and 0.1658 gram H_2O = 6.66 per cent. H.

II.—0.3705 gram dried substance gave 0.7048 gram CO_2 = 51.88 per cent. C, and 0.2232 gram H_2O = 6.69 per cent. H.

Nitrogen.—0.3923 gram dried substance gave 57.54 cc. N at 11° (barometer 753 mm. at 23°) = 17.48 per cent.

Sulphur.—0.6614 gram dried substance gave 0.0521 gram $BaSO_4$ = 1.08 per cent. S.

In order to facilitate a comparison of these analyses they have been brought together in the following table:

Proteid obtained from Flour by Direct Extraction with Dilute Alcohol.

	13.[1]	14.[1]	15.	16.	17.	18.	19.
C	..	..	52.52	52.77	52.67	52.55	52.74
H	..	..	6.78	6.78	6.70	6.85	6.77
N	17.18	17.26	17.64	17.77	17.66	17.94	17.62
S	..	..	1.08	1.26	1.22	1.21	1.23
O	..	..	21.98	21.42	21.75	21.45	21.64
			100.00	100.00	100.00	100.00	100.00

	20.	21.	23.	24.	25.	26.
C	52.39	52.84	53.02	..	52.33	52.38
H	6.93	6.81	6.79	..	6.91	7.13
N	17.31	17.67	17.32	17.69	17.70	17.82
S	1.38	1.11	1.05	.. }	23.06	22.67
O	21.99	21.57	21.82	.. }		
	100.00	100.00	100.00		100.00	100.00

Proteid obtained from Flour by Treatment with Dilute Alcohol after Extraction with 10-per cent. Sodium-Chloride Solution.

	27.	28.	29.	31.
C	52.69	52.72	52.71	52.65
H	6.84	6.86	6.81	6 83
N	17.73	17.89	17.75	17.79
S	1.02	0.95	1.10	1.08
O	21.72	21.58	21.63	21.65
	100.00	100.00	100.00	100.00

[1]Omitted in average.

Proteid extracted from Gluten by Dilute Alcohol.

	Flour, Spring Wheat.			Whole Spring Wheat Flour.			
	32.	**33.**	**34.**	**38.**	**39.**	**40.**	**43.**
C	52.58	52.68	52.84	52.90	52.89	53.16	52.24
H	6.67	6.78	7.18	6.99	6.87	6.83	6.71
N	17.65	17 65	17.57	17.52	18.06	17.75	17.57
S	1.08	1.09 }	22.41	1.43	0.92	0.96	1.08
O	22.02	21.80 }		21.16	21.26	21.30	22.40
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

		Winter.	
		41.	**42.**
C		52.82	52.68
H		6.88	6.81
N		17.55	17.63
S }		22.75	22.88
O }			
		100.00	100.00

Proteid extracted from Wheat Bran by Dilute Alcohol.

	35.	**36.**	**37.**
C	53.25	52.85	52.74
H	7.02	6.81	6.87
N	17.38	17.48	17.67
S	1.37 }	22.86	22.72
O	20.98 }		
	100.00	100.00	100.00

Average of the preceding Figures.

Carbon	52.72
Hydrogen	6.86
Nitrogen	17.66
Sulphur	1.14
Oxygen	21.62
	100.00

e.—Properties of Proteid extracted by Dilute Alcohol.

This substance, when dehydrated by absolute alcohol and thoroughly dried over sulphuric acid, forms a snow-white, friable mass which is easily reduced to a powder. If dried when moistened with dilute alcohol or water it is converted into an amorphous substance which resembles, in appearance, pure gelatin. When thoroughly dried in this condition it is rather more brittle

than gelatin. Dried in thin sheets it is perfectly clear and transparent. When treated in the cold with distilled water it becomes sticky and a part dissolves. If the water is warmed more dissolves, and on boiling much goes into solution. These solutions in warm water deposit a part of the dissolved substance on cooling, leaving the remainder dissolved. This solution in pure water is instantly precipitated by adding a very minute amount of sodium chloride.

In absolute alcohol this proteid is entirely insoluble, but dissolves on adding water, the solubility increasing with the addition of water up to a certain point, and then diminishing. The exact degree of solubility has not been determined for various strengths of alcohol, but mixtures of about 70 per cent. of alcohol and 30 per cent. of water dissolve the proteid in almost indefinite amount. From solutions in strong alcohol as well as from those in very weak alcohol the proteid is precipitated by adding a few drops of solution of sodium chloride, the completeness of the precipitation depending on the strength of the alcohol and the amount of salt added. The more the alcohol varies in strength from 70–80 per cent. the more completely is the substance precipitated.

In extremely dilute acids and alkalies this proteid is readily soluble, and is precipitated from such solutions on neutralization apparently unchanged either in properties or composition. With Millon's reagent, nitric acid and the biuret-test, the usual proteid reactions are given.

Dissolved in concentrated hydrochloric acid, a beautiful violet color is produced which develops slowly.

With warm 50-per cent. sulphuric acid a similar color is produced, which is greatly increased in intensity on boiling.

As already stated, Einhof, in 1805, was the first to discover that gluten contained a proteid substance soluble in dilute alcohol, to which the name of gliadin was afterward given by Taddei. Berzelius considered that this gliadin was a mixture of the body found by Einhof in rye with another proteid which he named mucin. Boussingault prepared for analysis the proteid extracted from gluten by diluted alcohol, and gave analyses of it in its impure state as well as purified by solution in acetic acid and precipitation with ammonia. The latter analysis will be given in the table which follows. De Saussure, like Berzelius, considered the substance extracted by alcohol to be a mixture of two proteid bodies which he called glutin and mucin. The latter he appeared to regard as

the same as Berzelius' mucin, yet its method of preparation was such as to render this improbable. This mucin was obtained by extracting the gluten with hot alcohol, adding an equal volume of water, concentrating the resulting solution to one-sixth the volume, cooling, decanting the mother-liquor, again adding water, concentrating and cooling. This process was repeated until no more substance separated on cooling. The resulting solution contained the mucin, which, however, De Saussure did not separate in a pure state. Liebig considered the alcohol-soluble portion of the gluten to be a casein-like compound of a proteid with some unrecognized vegetable acid. He gave to it the name of plant gelatin. He also speaks of mucin in such a way as to indicate his acceptance of De Saussure's statements regarding the existence of this body. He quotes analyses by Jones of the plant gelatin which will be found in the table following. Dumas and Cahours found that on extracting gluten with hot alcohol, a proteid substance was deposited on cooling, which they named plant casein. The concentrated filtrate from this body, on cooling, deposited a proteid which they called glutin. Analyses of both these bodies will be found in the table.

Mulder gave an analysis of " plant gelatin " which he extracted from gluten by treatment with alcohol and purification by repeated precipitations from solution in dilute alcohol by concentration and cooling.

Von Bibra, like Dumas and Cahours, considered that alcohol extracted from gluten both plant casein, which separated from a hot extract on cooling, and plant gelatin, which remained in solution. He gave the composition of these proteids as shown by the table and considered them to be isomers. Günsberg found that on boiling gluten with water a considerable amount of proteid matter was dissolved which, on cooling, was deposited. He regarded this as identical with Taddei's gliadin, and endorsed the latter's view that but two proteids were contained in gluten. Dumas' plant-casein he considered to be a portion of the insoluble part of the gluten which had escaped filtration. His analysis of the proteid extracted from gluten by boiling water, and of that obtained by boiling gliadin with water, are given in the table.

Ritthausen described three separate proteids which were extracted from gluten by dilute alcohol. These he separated from one another by fractional precipitation from alcoholic solutions of

various strengths, and also from solution in acetic acid by varying degrees of neutralization. The proteid soluble in the strongest alcohol he called gluten fibrin; that in less strong alcohol, plant gelatin, and the part soluble in the weakest alcohol, mucedin. Analyses of these products appear in the table. Later investigators have paid no attention to the proteids of wheat soluble in alcohol, with the exception of Sidney Martin, who calls the body thus extracted from gluten "insoluble phytalbumose." He further states that a careful repetition of Ritthausen's work failed to show the presence of any other proteid soluble in alcohol than this phytalbumose, and further, that extraction of the flour with alcohol of 76 to 80 per cent., applied before the addition of water, failed to remove any proteid. This latter statement is in direct contradiction to the experience of the writers, who have never failed to obtain the proteid in this way, and in amounts equal to that extracted from the gluten. As Martin gives no details of his operations, no explanation can be offered.

In the following table is given the analyses of the various investigators just named :

	Boussingault. Gliadin.	Jones. Plant Gelatin.	Dumas and Cahours. Casein.	Glutin.	Mulder. Plant Gelatin.	Von Bibra. Plant Gelatin.
C	52.3	54.44[1]	53.46	53.27	54.85	53.57
H	6.5	7.42	7.13	7.17	7.05	7.12
N	18.9	15.98	16.04	15.94	15.71	15.57
S	..	..	..	..	0.60	0.88
O	22.3	22.16	23.37	23.62	21.79	22.86
	100.00	100.00	100.00	100.00	100.00	100.00

	Günsberg. Plant Gelatin		Ritthausen. Glutin Fibrin.	Plant Gelatin.	Mucedin.
C	52.68	52.65	54.31	52.76	54.11
H	6.77	6.88	7.18	7.10	6.90
N	17.76	17.45	16.89	18.01	16.63
S	..	..	1.01	0.85	0.88
O	22.79	23.02	20.61	21.28[2]	21.48
	100.00	100.00	100.00	100.00	100.00

If Günsberg's and Ritthausen's analyses of plant gelatin are compared with those of the writers, it will be seen that they are in close agreement. The analyses of the predecessors of Günsberg differ very materially, both from each other and those of later

Recalculated for an atomic weight of carbon = 12.
Given by Ritthausen as 21.37.

investigators. This is partly due to the imperfect methods of analysis and partly to insufficient purification of the preparations. As details of the work of these earlier chemists are lacking, a fair criticism of their results cannot be made. It may be said, however, that their analyses are not corroborated by the work done since their publication, and that they are undoubtedly incorrect. Ritthausen's composition of plant gelatin is corroborated in the main by the writers' analyses, and there can no longer be any doubt that it represents nearly the true composition of this proteid. We have, however, been unable to obtain any evidence of the existence of the two remaining proteids, gluten fibrin and mucedin. The numerous attempts to precipitate fractionally the alcohol-soluble proteid, although yielding products soluble in every strength of alcohol, has, in every case where the conditions allowed of preparing the proteid free from fat and other foreign bodies, resulted in giving preparations whose properties and composition were identical. It is our opinion that Ritthausen's gluten fibrin and mucedin are simply impure or altered preparations of his plant gelatin. Sidney Martin holds the same opinion, and Günsberg concluded that gliadin was the only proteid dissolved by alcohol. The mucin of Berzelius and De Saussure must also be considered impure plant gelatin, as we can find no evidence of their existence as definite chemical substances. Dumas and Cahours' casein, Günsberg considers to be a part of the insoluble portion of the gluten which had escaped filtration.

The writers consider this to be a part of the gliadin which, owing to the strength of the alcohol used, was more soluble when *hot* than when cold. We are therefore forced to conclude that in the wheat kernel only one proteid soluble in dilute alcohol exists, and that this is one of the constituents of the gluten. That it occurs in the same form in the gluten as in the seed and that there is no change, so far as this body is concerned, caused by contact of the wheat flour with water, has frequently been suggested during the past few years.

This body was first discovered by Einhof and named by Taddei gliadin on account of its resemblance to glue. Since then it has been named by Liebig plant gelatin, by Dumas and Cahours glutin, and, contaminated with various impurities, it has been called by De Saussure and Berzelius mucin and by Ritthausen gluten fibrin and mucedin. It would appear to the writers there-

fore to be proper that we should return to the original and appropriate name and henceforth call it gliadin.

This proteid is entirely distinct in composition and properties from the alcohol-soluble proteids of the maize and oat kernel.

V.—Proteid insoluble in Water, Saline Solutions, and Alcohol.

As already stated, extraction with the above-named solvents, applied successively, removed but a part of the total proteid contained in the wheat kernel, that remaining being soluble only in dilute acids and alkalies. The following extractions were next made to determine the nature of this body.

a.—*Proteid extracted by Dilute Potash Solution after extracting the Flour with* 10-*per cent. Sodium-Chloride Brine and then with Dilute Alcohol.*

After completely extracting from 4000 grams "straight flour" all the proteids soluble in 10-per cent. sodium-chloride solution, the residue was freed wholly from proteids soluble in cold alcohol of 0.90 sp. gr. The resulting residue was then extracted twice with a large quantity of $\frac{1}{10}$-per cent. potash solution. After standing three days at a temperature of 5° with frequent stirring this extract was filtered off and allowed to stand in a cold room until the greater part of the fine starch and other impurities which had escaped filtration had settled. The solution, which was still turbid, was decanted from the sediment and neutralized as exactly as possible with $\frac{2}{10}$-per cent. hydrochloric acid, thereby producing a precipitate which settled rapidly, leaving the filtrate milky in appearance. This precipitate, after decanting the solution, was dissolved in $\frac{2}{10}$-per cent. potash water and set aside to deposit the suspended impurities. After decantation from the sediment which resulted, the solution was filtered, but almost nothing was thus removed. It was then neutralized with $\frac{2}{10}$-per cent. hydrochloric acid and the precipitate produced washed by decantation, first with water and then with dilute alcohol, absolute alcohol and ether. No attempt was made in this case to obtain the whole of the proteid soluble in alkali, as the difficulties presented by slow and imperfect filtration rendered this impossible. 13 grams of substance were obtained which, after drying over sulphuric acid, formed a brownish, horny mass. This, preparation **44**, when dried at 110°, gave the following results on analysis:

WHEAT PROTEID, *Preparation* 44.

		Ash-free.
Carbon	52.47	52.91
Hydrogen	6.75	6.81
Nitrogen	15.51	15.65
Sulphur	0.86	0.86
Oxygen	..	23.77
Ash	0.88	..
		100.00

Ash.—0.3919 gram substance dried at 110° gave 0.0073 gram ash = 0.88 per cent.

Carbon and Hydrogen.—0.3561 gram dried substance gave 0.6851 gram CO_2 = 52.47 per cent. C, and 0.2163 gram H_2O = 6.75 per cent. H.

Nitrogen.—0.3102 gram dried substance gave 38.82 cc. N at 6° (barometer 769.5 mm. at 22°) = 15.51 per cent.

Sulphur.—0.6108 gram dried substance gave 0.0384 gram $BaSO_4$ = 0.86 per cent. S.

Subsequent preparations of this body led to the idea that it was far from pure, this supposition being supported by the fact that the final solution from which it had been precipitated was turbid. The remainder of the preparation was then dissolved as completely as possible in $\frac{2}{10}$-per cent. potash solution, and by repeated filtration through very dense filter-paper obtained perfectly clear. A considerable insoluble residue remained, which appeared to consist largely of the coagulated form of this proteid. This residue was washed by decantation with water, alcohol and ether, and dried over sulphuric acid and then at 110° C. It was found to contain but 13.68 per cent. of nitrogen, showing that the preparation **44** contained much non-nitrogenous matter. The filtration of the dissolved proteid proceeded very slowly, so that it was deemed best to conduct this operation in a refrigerator at a temperature near 0°. A portion of the filtrate first obtained was removed, precipitated by $\frac{2}{10}$-per cent. hydrochloric acid, washed with water, alcohol and ether, and the preparation, **45**, analyzed with the following results. A second portion similarly yielded preparation **46**.

WHEAT PROTEID, *Preparation* 45.

	I.	II.	Average.	Ash-free.
Carbon	51.10	..	51.10	52.29
Hydrogen	6.46	..	6.46	6.61
Nitrogen	17.01	..	17.01	17.41
Sulphur	0.91	0.92	0.92	0.94
Oxygen	..	..	..	22.75
Ash	2.28	..	..	..
				100.00

Ash.—0.3233 gram substance dried at 110° gave 0.0074 gram ash = 2.28 per cent.

Carbon and Hydrogen.—0.2468 gram dried substance gave 0.4624 gram CO_2 = 51.10 per cent. C, and 0.1435 gram H_2O = 6.46 per cent. H.

Nitrogen.—0.2439 gram dried substance gave 35.23 cc. N at 16° (barometer 758 mm. at 28°) = 17.01 per cent.

Sulphur, I.—0.3218 gram dried substance gave 0.0213 gram $BaSO_4$ = 0.91 per cent. S.

II.—0.4833 gram dried substance gave 0.0325 gram $BaSO_4$ = 0.92 per cent. S.

WHEAT PROTEID, *Preparation* 46.

		Ash-free.
Nitrogen	17.17	17.33
Ash	0.97	..

Ash.—0.4214 gram substance dried at 110° gave 0.0041 gram ash = 0.97 per cent.

Nitrogen.—0.3184 gram dried substance gave 46.06 cc. N at 16° (barometer 763.7 mm. at 23°) = 17.17 per cent.

These results show that it is absolutely necessary to filter the solution of this body in potash water *perfectly clear* before the final precipitation, since otherwise a considerable amount of non-nitrogenous matter will be precipitated with it. Another extraction was made by treating 200 grams of "patent flour" from spring wheat with 10-per cent. sodium-chloride solution, added in small quantities so as to make a dough. This dough was then washed with 10-per cent. sodium-chloride brine until nearly all the starch was removed and a gluten obtained similar in all respects to that resulting from treating the flour with water. This gluten was then chopped fine, thoroughly extracted with alcohol of sp. gr. 0.90, and then dissolved at 20° in $\frac{1}{10}$-per cent. potash water. The resulting solution was filtered, but as only a part of the impurities was thus removed, the filtrate was placed in an ice-box in shallow dishes and allowed to deposit a considerable part of the suspended matter. The solution which was decanted from the sediment was only slightly turbid, and was then precipitated by neutralizing with $\frac{2}{10}$-per cent. hydrochloric acid. The precipitate filtered off was washed by decantation with water, extracted thoroughly with dilute alcohol, digested with absolute alcohol and then with ether, and dried over sulphuric acid. This preparation, 47, was a snow-white, light, porous mass, easily reduced to a powder. It had the following composition:

WHEAT PROTEID, *Preparation* **47.**

	I.	II.	Average.	Ash-free.
Carbon	..	52.18	..	52.50
Hydrogen	..	6.90	..	6.94
Nitrogen	17.11	16.90	17.01	17.22
Sulphur	..	1.00	..	1.00
Oxygen	..	..	..	22.34
Ash	..	0.63	..	..
				100.00

Ash.—0.5626 gram substance dried at 110° gave 0.0038 gram ash $=$ 0.63 per cent.

Carbon and Hydrogen.—0.3050 gram dried substance gave 0.5836 gram $CO_2 = 52.18$ per cent. C, and 0.1890 gram $H_2O = 6.90$ per cent. H.

Nitrogen, I.—0.3666 gram dried substance gave 53.15 cc. N at 15° (barometer 756.5 mm. at 22°) $=$ 17.11 per cent.

II.—0.6033 gram dried substance gave 49.33 cc. N at 15° (barometer 759.3 mm. at 21°) $=$ 16.90 per cent.

Sulphur.—0.5449 gram dried substance gave 0.0400 gram $BaSO_4 = 1.00$ per cent. S.

b.—Proteid extracted by Dilute Potash Water after Treatment of the Dough with Water and Extraction with Dilute Alcohol.

2000 grams of "straight flour" from spring wheat were made into a dough with distilled water, and this was washed with river water until the gluten was freed as completely as possible from starch. This gluten was then extracted with 75-per cent. alcohol as long as anything was removed. The insoluble residue was dissolved in $\frac{1.5}{100}$-per cent. potash water and the resulting solution allowed to stand in a cold room for 48 hours. The solution was thus freed from but a part of the suspended matter. After decanting from the sediment the solution was neutralized with dilute hydrochloric acid, the precipitate produced, washed several times by decantation with water, thoroughly extracted with alcohol of 0.90 sp. gr., then with stronger alcohol and finally with absolute alcohol and with ether.

The precipitate was again dissolved in $\frac{1}{10}$-per cent. potash solution and allowed to stand over night. It was then filtered and a part of the clear filtrate first obtained was precipitated by neutralization with $\frac{2}{10}$-per cent. hydrochloric acid. This precipitate was washed with water, alcohol, absolute alcohol and ether, yielding preparation **48.** A part of this preparation **48** was redissolved in

$\frac{2}{10}$-per cent. potash water and found to contain a considerable amount of substance which had become insoluble in consequence of drying. This insoluble portion was filtered off, washed with water, alcohol and ether, and gave preparation **49**. The filtrate from this substance was precipitated with $\frac{2}{10}$-per cent. hydrochloric acid, and the precipitate filtered off and washed with water, alcohol and ether. Through an accident this preparation dried on the filter and could not be removed from the paper. It was then again dissolved in dilute potash water and treated exactly as before, yielding preparation **50**. The following analyses show the composition of these three preparations:

WHEAT PROTEID, *Preparation* **48**.

	I.	II.	Average.	Ash-free.
Carbon	51.59	..	51.59	52.32
Hydrogen	6.72	..	6.72	6.82
Nitrogen	17.34	17.39	17.37	17.61
Sulphur ⎱ Oxygen ⎰	..	..	..	23.25
Ash	1.40	..	..	..
				100.00

Ash.—0.9136 gram substance dried at 110° gave 0.0128 gram ash = 1.40 per cent.

Carbon and Hydrogen.—0.3983 gram dried substance gave 0.7535 gram CO_2 = 51.59 per cent. C, and 0.2410 gram H_2O = 6.72 per cent. H.

Nitrogen, I.—0.3407 gram dried substance gave 50.14 cc. N at 16° (barometer 757 mm. at 18°) = 17.34 per cent.

II.—0.3542 gram dried substance gave 51.34 cc. N at 13° (barometer 764 mm. at 24°) = 17.39 per cent.

WHEAT PROTEID, *Preparation* **49**.

	I.	II.	Average.	Ash-free.
Carbon	50.79	..	50.79	52.87
Hydrogen	6.62	..	6.62	6.88
Nitrogen	16.38	16.38	16.38	17.05
Sulphur ⎱ Oxygen ⎰	..	..	..	23.20
Ash	3.94	..	3.94	..
				100.00

Ash.—0.8060 gram substance dried at 110° C. gave 0.0318 gram ash = 3.94 per cent.

Carbon and Hydrogen.—0.3671 gram dried substance gave 0.6836 gram CO_2 = 50.79 per cent. C, and 0.2186 gram H_2O = 6.62 per cent. H.

Nitrogen, I.—0.4013 gram dried substance gave 55.56 cc. N at 15° (barometer 758.4 mm. at 22°) = 16.38 per cent.

II.—0.3166 gram dried substance gave 43.74 cc. N at 13° (barometer 754.4 mm. at 21.5°) = 16.38 per cent.

WHEAT PROTEID, *Preparation* 50.

	I.	II.	Average.	Ash-free.
Carbon	51.50	51.37	51.44	52.62
Hydrogen	6.70	6.57	6.64	6.80
Nitrogen	16.70	..	16.70	17.08
Sulphur } Oxygen }	..	..	..	23.50
Ash	2.25	..	..	..
				100.00

Ash.—0.4428 gram substance dried at 110° gave 0.0100 gram ash = 2.25 per cent.

Carbon and Hydrogen, I.—0.3955 gram dried substance gave 0.7469 gram CO_2 = 51.50 per cent. C, and 0.2383 gram H_2O = 6.70 per cent. H.

II.—0.3363 gram dried substance gave 0.6335 gram CO_2 = 51.37 per cent. C, and 0.1986 gram H_2O = 6.57 per cent. H.

Nitrogen.—0.3918 gram dried substance gave 54.36 cc. N at 13° (barometer 766.5 mm. at 24°) = 16.70 per cent.

Another lot of gluten made from 1000 grams of "straight flour" was treated in exactly the same way as that last described. This gluten was thoroughly extracted with alcohol of 0.90 sp. gr. and the residue dissolved in about 500 cc. of $\frac{2}{10}$-per cent. potash water. After standing over night the very turbid liquid was decanted from the sediment which had formed, and treated with very dilute acetic acid added to slightly acid reaction. The precipitate produced was washed with water, alcohol, and ether and dissolved again in $\frac{2}{10}$-per cent. potash water. The resulting solution, filtered perfectly clear, was precipitated with $\frac{2}{10}$-per cent. hydrochloric acid, washed by decantation with water, then with dilute alcohol, increased gradually in strength up to absolute alcohol, and finally with ether. Dried over sulphuric acid, a pure white, light mass was obtained. This, preparation 51, was analyzed with the following results :

WHEAT PROTEID, *Preparation* 51.

	I.	II.	Average.	Ash-free.
Carbon	52.07	52.23	52.15	52.54
Hydrogen	6.71	6.88	6.80	6.85
Nitrogen	17.23	17.42	17.33	17.46
Sulphur	1.07	..	1.07	1.07
Oxygen	..	..	..	22.08
Ash	0.74	0.76	0.75	..
				100.00

Ash, I.—0.8215 gram substance dried at 110° gave 0.0061 gram ash = 0.74 per cent.

II.—0.3008 gram dried substance gave 0.0023 gram ash = 0.76 per cent.

Carbon and Hydrogen, I.—0.3254 gram dried substance gave 0.6213 gram CO_2 = 52.07 per cent. C, and 0.1963 gram H_2O = 6.70 per cent. H.

II.—0 1690 gram dried substance gave 0.3237 gram CO_2 = 52.23 per cent. C, and 0.1048 gram H_2O = 6.88 per cent. H.

Nitrogen, I.—0.3715 gram dried substance gave 53.15 cc. N at 12° (barometer 764 mm. at 20°) = 17.23 per cent.

II.—0.2906 gram dried substance gave 42.23 cc. N at 11° (barometer 757.3 mm. at 20°) = 17.42 per cent.

Sulphur.—0.3307 gram dried substance gave 0.0258 gram $BaSO_4$ = 1.07 per cent. S.

Again gluten was prepared in the usual manner and extracted with alcohol until everything soluble in that reagent was removed. The residue was then dissolved in $\frac{2}{10}$-per cent. potash water and, in order to carry the operation to an end as rapidly as possible, the solution was at once thrown into a filter. As soon as the filtrate ceased to pass through turbid it was returned to the funnel and the filtration continued in an ice-chest. 20 hours after the first solution of the substance in potash water a considerable proportion of the solution was obtained perfectly clear. This was then precipitated with $\frac{2}{10}$-per cent. hydrochloric acid and treated in the usual manner, giving preparation **52**.

The filtration of the potash solution was continued in the ice-chest and after three days the rest of the solution was obtained clear. This was precipitated and treated in the same manner as the preceding, yielding preparation **53**. In this way it was hoped to learn the effect on this substance of prolonged solution in dilute potash water. The composition of these proteids is shown by the following analyses:

WHEAT PROTEID, *Preparation* **52**.

		Ash-free.
Carbon	52.07	52.38
Hydrogen	6.77	6.81
Nitrogen	17.49	17.59
Sulphur	1.24	1.24
Oxygen	..	21.98
Ash	0.61	..
		100.00

Ash.—0.3429 gram substance dried at 110° gave 0.0021 gram ash = 0.61 per cent.

Carbon and Hydrogen.—0.3781 gram dried substance gave 0.7220 gram CO_2 = 52.07 per cent. C, and 0.2306 gram H_2O = 6.77 per cent. H.

Nitrogen.—0.2616 gram dried substance gave 38.22 cc. N at 14° (barometer 765 mm. at 24°) = 17.49 per cent.

Sulphur.—0.1545 gram dried substance gave 0.0140 gram $BaSO_4$ = 1.24 per cent. S.

WHEAT PROTEID, *Preparation* 53.

Nitrogen   17.10

Nitrogen.—0.1569 gram dried substance gave 22.65 cc. N at 15° (barometer 758.6 mm. at 21°) = 17.10 per cent.

From those figures it is evident that but little loss of nitrogen is caused by prolonging the solution in dilute potash water.

In order to make sure that this conclusion was correct the experiment was repeated in the same way. During the three days in which the second part of the potash solution was in the ice-box the ice melted and at the conclusion the temperature reached 20°. The two preparations thus obtained, numbered respectively **54** and **55**, contained the following amounts of nitrogen:

WHEAT PROTEID, *Preparation* 54.

		Ash-free.
Nitrogen	17.32	17.53
Ash	1.23	..

Ash.—0.3654 gram substance dried at 110° gave 0.0045 gram ash = 1.23 per cent.

Nitrogen.—0.2107 gram dried substance gave 30.42 cc. N at 14° (barometer 765.3 mm. at 25°) = 17.32 per cent.

WHEAT PROTEID, *Preparation* 55.

		Ash-free.
Nitrogen	17.50	17.53
Ash	0.16	..

Ash.—0.4200 gram substance dried at 110° gave 0.0007 gram ash = 0.16 per cent.

Nitrogen.—0.2200 gram dried substance gave 32.12 cc. N at 15° (barometer 764.8 mm. at 21°) = 17.50 per cent.

Another preparation of this substance was made by completely extracting 200 grams of "patent flour" (from spring wheat) with large quantities of alcohol of 0.90 sp. gr. The flour was then

washed with absolute alcohol and air-dried. The dry material
was then powdered and made into a dough with distilled water.
The resulting dough had considerable coherence, showing that
the proteid insoluble in alcohol played an important part in its
formation. This dough was then washed on a fine hair-sieve
under a stream of running water, but no coherent gluten resulted.
The washings were then allowed to settle and the sediment, after
decanting the solution, was treated with $\frac{2}{10}$-per cent. potash. The
solution so obtained after standing over night was decanted from
the sediment and precipitated with $\frac{2}{10}$-per cent. hydrochloric acid
and the separated proteid allowed to settle. The solution was
then decanted, the precipitate dissolved in $\frac{2}{10}$-per cent. potash
water and filtered clear in the ice-box. The filtered solution was
then precipitated and the separated substance treated in the usual
manner. This preparation, **56**, contained the following amount of
nitrogen :

WHEAT PROTEID, *Preparation* **56**.

	I.	II.	Average.	Ash-free.
Nitrogen	17.04	16.93	16.99	17.20
Ash	1.22	..	..	..

Ash.—0.5740 gram substance dried at 110° gave 0.0070 gram ash = 1.22
per cent.

Nitrogen, I.—0.3544 gram dried substance gave 50.74 cc. N at 16° (baro-
meter 765.2 mm. at 22°) = 17.04 per cent.

II.—0.3600 gram dried substance gave 51.34 cc. N at 17° (barometer 766.2
mm. at 21°) = 16.93 per cent.

In order to learn whether any change in the proteids occurred
in consequence of contact with aqueous solutions before extracting
with potash water, the following experiment was made.

1000 grams of "straight flour" from spring wheat were
repeatedly extracted with alcohol of 0.90 sp. gr., and after remov-
ing everything soluble in that liquid the alcohol was squeezed out
as completely as possible in a screw press and the residue
extracted with $\frac{2}{10}$-per cent. potash water. It was found impossible
to separate the solution from the undissolved portion of the meal
either by filtration or subsidence, on account of the presence of
gummy matter. An equal volume of alcohol of sp. gr. 0.820 was
therefore added, and on long standing the insoluble substance
gradually settled, leaving a comparatively clear, yellow solution.
This was then syphoned off and filtered. On account of its

gummy character it filtered very slowly. The clear solution finally obtained was then precipitated with $\frac{2}{10}$-per cent. hydrochloric acid, the precipitate filtered off and dissolved in $\frac{2}{10}$-per cent. potash water. The solution so obtained was filtered clear and precipitated with $\frac{2}{10}$-per cent. hydrochloric acid, the resulting precipitate washed by decantation with water, alcohol, at first dilute then gradually increased to absolute, and finally with ether. Preparation **57** was thus obtained, having the following composition:

WHEAT PROTEID, *Preparation* **57.**

		Ash-free.
Carbon	52.14	52.19
Hydrogen	6.91	6.92
Nitrogen	17.54	17.56
Sulphur ⎰ Oxygen ⎱	..	23.33
Ash	0.10	..
		100.00

Ash.—0.7996 gram substance dried at 110° gave 0.0008 gram ash = 0.10 per cent.

Carbon and Hydrogen.—0.3426 gram dried substance gave 0.6550 gram CO_2 = 52.14 per cent. C, and 0.2132 gram H_2O = 6.91 per cent. H.

Nitrogen.—0.2671 gram dried substance gave 39.21 cc. N at 15° (barometer 766 mm. at 22°) = 17.54 per cent.

This analysis shows that the same proteid is extracted by potash water from the flour which has not been in contact with water, as was obtained in the other experiments.

c.—*Proteid extracted by Dilute Potash Water after Complete Extraction, with Dilute Alcohol, of Gluten from Whole Wheat Flour.*

1000 grams of flour made by grinding the *entire* kernel of spring wheat were made into a dough, washed with water till free from starch, and the gluten obtained extracted thoroughly with dilute alcohol. The residue was then dissolved in $\frac{2}{10}$-per cent. potash water, and after the resulting solution had stood for some time it was decanted from the sediment and precipitated by $\frac{2}{10}$-per cent. hydrochloric acid. The precipitate was washed by decantation with water, thoroughly extracted with dilute alcohol and then with absolute alcohol, and finally with ether, and then redissolved in $\frac{2}{10}$-per cent. potash water.

The solution, after filtering perfectly clear, was precipitated and the precipitate treated in the same manner as all the preceding preparations.

When analyzed it was found to have the following composition :

WHEAT PROTEID, *Preparation* 58.

	I.	II.	Average.	Ash-free.
Carbon	51.59	51.67	51.63	52.19
Hydrogen	6.85	6.87	6.86	6.93
Nitrogen	17.21	17.32	17.27	17.45
Sulphur	0.89	..	0.89	0.90
Oxygen	..	..	..	23.43
Ash	1.07	..	..	..
				100.00

Ash.—0.4095 gram substance dried at 110° gave 0.0043 gram ash = 1.07 per cent.

Carbon and Hydrogen, I.—0.2532 gram dried substance gave 0.4790 gram $CO_2 = 51.59$ per cent. C, and 0.1561 gram $H_2O = 6.85$ per cent. H.

II.—0.2469 gram dried substance gave 0.4678 gram $CO_2 = 51.67$ per cent. C, and 0.1517 gram $H_2O = 6.87$ per cent. H.

Nitrogen, I.—0.3141 gram dried substance gave 46.07 cc. N at 19° (barometer 763.2 mm. at 26°) = 17.21 per cent. N.

II.—0.1350 gram dried substance gave 19.75 cc. N at 19° (barometer 769 mm. at 19°) = 17.32 per cent.

Sulphur.—0.6637 gram dried substance gave 0.0433 gram $BaSO_4 = 0.89$ per cent. S.

The filtrate from this preparation as well as all the others previously described contained a small amount of proteid matter.

This was then treated with a solution of copper sulphate and the small precipitate thereby produced filtered off, washed with water, alcohol and ether, and found to contain the following amount of nitrogen :

WHEAT PROTEID, *Preparation* 59.

		Ash-free.
Nitrogen	13.28	17.45
Ash	23.88	..

Ash.—0.2542 gram substance dried at 110° gave 0.0607 gram ash = 23.88 per cent.

Nitrogen.—0.3849 gram dried substance gave 43.24 cc. N at 19° (barometer 768.2 mm. at 20°) = 13.28 per cent.

In the same way as 58 a preparation of this proteid was made from flour from the *entire* kernel of winter wheat. The composition of this preparation is shown by the accompanying figures.

WHEAT PROTEID, *Preparation* 60.

	I.	II.	Average.	Ash-free.
Carbon	51.71	..	51.71	52.03[1]
Hydrogen	6.79	..	6.79	6.83
Nitrogen	17.32	17.44	17.38	17.48
Sulphur ⎰ Oxygen ⎱	..	..	..	23.66
Ash	0.62	..	0.62	..
				100.00

Ash.—0.4217 gram substance dried at 110° gave 0.0026 gram ash = 0.62 per cent.

Carbon and Hydrogen.—0.2702 gram dried substance gave 0.1652 H_2O = 6.79 per cent. H, and 0.5123 gram CO_2 = 51.71 per cent. C.

Nitrogen, I.—0.3346 gram dried substance gave 48.09 cc. N at 11.5° (barometer 762 mm. at 17.5°) = 17.32 per cent.

II.—0.4140 gram dried substance gave 60.52 cc. N at 11° (barometer 754 mm. at 22°) = 17.44 per cent.

A second portion of the same solution from which preparation **60** had been precipitated was obtained two days later. This was then treated in the same way and yielded preparation **61**, which was found to have the following composition :

WHEAT PROTEID, *Preparation* 61.

		Ash-free.
Carbon	51.17	52.44
Hydrogen	6.70	6.86
Nitrogen	17.35	17.81
Sulphur ⎰ Oxygen ⎱	..	22.89
Ash	2.62	..
		100.00

Ash.—0.3924 gram substance dried at 110° gave 0.0103 gram ash = 2.62 per cent.

Carbon and Hydrogen.—0.3320 gram dried substance gave 0.2019 gram H_2O = 6.70 per cent., and 0.6229 gram CO_2 = 51.17 per cent. C.

Nitrogen.—0.3135 gram dried substance gave 45.17 cc. N at 10° (barometer 757.7 mm. at 21°) = 17.35 per cent.

If we omit preparations **44** and **47** on account of being obtained from unfiltered solutions, **49** as an altered and insoluble product, **50** as having been subjected to an exceedingly prolonged action of an alkaline solution, and **53**, as no correction for ash could be

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[1] Trace of unburned carbon left in boat.

made, we will then have in the following table the analyses which in the opinion of the writers most nearly represent the true composition of this proteid.

PROTEID OF THE WHEAT KERNEL SOLUBLE ONLY IN DILUTE ACIDS AND ALKALIES.

	45.	**48.**	**51.**	**52.**	**57.**	**58.**	**60.**	**61.**
C	52.29	52.32	52.54	52.38	52.19	52.19	52.03[1]	52.44
H	6.61	6.82	6.85	6.81	6.92	6.93	6.83	6.86
N	17.41	17.61	17.46	17.59	17.56	17.45	17.48	17.81
S	0.94 }	23.25	1.07	1.24 }	23.33	23.43	23.66	22.89
O	22.75 }		22.08	21.98 }				
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	46.	**54.**	**55.**	**56.**	**59.**
N	17.33	17.53	17.53	17.20	17.45

	Average.
Carbon	52.34
Hydrogen	6.83
Nitrogen	17.49
Sulphur	1.08
Oxygen	22.26
	100.00

Taddei was the first to describe this proteid, which remains after extraction of the gluten with dilute alcohol. He gave it the name of zymom. Berzelius considered Taddei's zymom to be identical with coagulated albumin. Liebig called this substance plant fibrin, and regarded it as the same as blood fibrin. He quoted analyses by Jones and Scherer, which will be found in the table following. Scherer subsequently published another analysis differing somewhat from that given by Liebig. Dumas and Cahours claim priority to Liebig in the use of this name, plant fibrin, one of them having previously used it in his lectures. They prepared their plant fibrin by washing gluten thoroughly with water, extracting this completely with alcohol and with ether, and then digesting the residue with diastase until starch was removed. The composition given by them for this body will be found in the annexed table.

Von Bibra analyzed "plant fibrin" obtained by boiling gluten with dilute alcohol as long as anything was removed. Ritthausen,

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[1] Omitted in average.

whose methods the writers have employed in preparing this substance, obtained a number of preparations of this proteid to which he gave the name "gluten casein." He gave the figures to be found in the table as expressing most nearly the true composition of this body. Weyl and Bischoff considered that gluten resulted through the action of some ferment, present in the seed, upon a myosin-like globulin, and that its constituent proteids were consequently not those previously existing in the grain. Martin held the same view. He rejected Ritthausen's name "gluten casein," and designated this substance as "gluten fibrin," a name used by Ritthausen for a body which he described as existing in gluten, soluble in diluted alcohol.

Chittenden and Smith made many preparations of "gluten casein," following Ritthausen's directions. The alkaline solution of the portion of the gluten insoluble in dilute alcohol they did not filter, but allowed to stand at rest for 48 hours, in order to deposit solid particles. The solution, which was then slightly turbid, was precipitated by neutralization with acetic acid. The average of eight analyses is given in the table.

EARLIER ANALYSES OF THE PROTEID SOLUBLE ONLY IN DILUTE ACIDS AND ALKALIES.

	Jones.	Scherer.		Dumas and Cahours.		von Bibra.	Ritthausen.	Chittenden and Smith.
		1.	**2.**	**1.**	**2.**			
C	52.79	54.60	52.34	53.37	53.23	53.57	52.94	52.87
H	7.02	7.45	7.13	7.02	7.01	6.95	7.04	6.99
N	15.59	15.81	15.36	16.00	16.41	15.70	17.14	15.86
S O	} 24.61	22.14	25.17	23.64	23.35	1.02 22.76	0.96 21.92	1.17 23.11
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

There can be no doubt that the analyses given by these chemists, with the exception of Ritthausen, and Chittenden and Smith, are incorrect, for the substance analyzed by each contained a large part of the impurities of the gluten, since after extraction with alcohol the residue was not dissolved in any solvent and the starch, bran, etc., contained in it filtered off. Ritthausen's figures are the average of two analyses of preparations obtained from solutions in $\frac{2}{10}$-per cent. potash water which had been filtered, one perfectly clear, giving a product containing 17.21 per cent. N; the other very nearly clear and containing 17.08 per cent. N.

From a solution clarified by subsidence, which, however, was still turbid, he obtained a preparation which agrees very well with the analyses of Chittenden and Smith and also with the writers' preparation 44. To afford a ready comparison these three analyses are here brought together:

	Chittenden and Smith.	Osborne. 44.	Ritthausen.
C	52.87	52.91	52.66
H	6.99	6.81	6.76
N	15.86	15.65	16.17
S	1.17	1.06	0.86
O	23.11	23.77	23.35
	100.00	100.00	100.00

These figures show plainly that the alkaline solution of the gluten after extraction with cold dilute alcohol contains something which is not removed by subsidence, but requires filtration through very dense paper to effect its separation. In preparing from commercial gluten a large quantity of the proteids contained in it the writer obtained from the ether washings a considerable amount of phytocholesterin and lecethin together with fat. It is probable that all these bodies are held suspended in the solution by aid of the dissolved proteid as an emulsion, and can only be removed by precipitating the first solution in potash water, extracting the precipitate with alcohol and ether, redissolving, and filtering the resulting solution perfectly clear. The first alkaline solution before precipitating and extracting with alcohol and ether cannot be filtered, as it either passes through the paper turbid or does not run through at all.

It is of course unnecessary to consider Berzelius' theory of the identity of this body with coagulated albumin, or Liebig's and Dumas and Cahours', of its identity with blood fibrin. The theories of Weyl and Bischoff and of Martin, however, deserve attention, as their views are at present very generally accepted by physiological chemists. It will not be desirable here to enter into a consideration of these views, as they will be discussed later in connection with gluten and its formation. On the ground of priority and the fact that the relations to animal proteids which gave rise to the various names subsequently applied to this body, have been proved to have no foundation, it would be desirable to return to Taddei's original name and in future call this proteid

zymom. Unfortunately this name is derived from the Greek word ζύμη, a ferment, and as the results of this investigation show that the supposed ferment-changes do not occur in the formation of gluten, this name is undesirable. As this proteid is especially characteristic of gluten, it seems appropriate to call it *glutenin*, a name suggested to us by Professor S. W. Johnson.

d.—*Properties of Glutenin.*

Characteristic reactions of a proteid body which can be dissolved only in dilute acids or alkalies are necessarily very few in number. In distilled water, preparations obtained as described, after drying over sulphuric acid, were found to yield a very little substance, which could be detected by caustic potash and cupric sulphate. If the water was warmed slightly the reaction was more pronounced. Diluted alcohol also dissolved a minute amount of proteid matter in the cold, and when heated to boiling, a much greater quantity. It is of course questionable whether the minute amount of substance dissolved by water and by alcohol was not due to a trace of gliadin which had not been completely extracted in the process of preparing the glutenin. The fact that the solution in hot alcohol began to precipitate at once on cooling, and that especial care had been taken in all cases completely to extract all gliadin, makes it most probable that the glutenin is slightly soluble in water and in alcohol, especially if these are warmed.

In very dilute alkalies, as $\frac{1}{10}$-per cent. potash solution, and in very dilute acids, as $\frac{2}{10}$-per cent. hydrochloric acid, this substance, after dehydration with absolute alcohol and drying over sulphuric acid, is slowly soluble, with the exception of a greater or less amount of insoluble residue, depending on the circumstances of its preparation. When freshly precipitated and in the hydrated condition it is extremely soluble in the slightest excess of caustic alkali, and in a somewhat greater but still very slight excess of acid. In this condition it is also soluble in the slightest excess of carbonate-of-soda solution or ammonia. Dried over sulphuric acid it dissolves partly in $\frac{5}{10}$-per cent. sodium-carbonate solution.

Dissolved in concentrated hydrochloric acid it gives a solution slightly yellowish at first, but becoming a deep violet color on standing. In sulphuric acid diluted with an equal volume of water the solution is brownish in color after boiling, and remains

clear when diluted.   The undiluted solution, on standing, retains its brown color.

A comparison of the analyses of this proteid with those of gliadin shows a very close agreement. As it is well known that many if not most proteids pass readily into conditions in which their solubility is greatly changed without changing their composition to an extent detectable by the most careful analysis, it would seem proper to consider this body as an altered form of gliadin in which its solubility was changed in much the same way as the so-called albuminates derived from globulins.   The writer has shown that the albuminates from several of the crystallizable globulins, while insoluble in cold 10-per cent. sodium-chloride solution, are readily soluble at 50°, and separate again on cooling in a crystalline form. In the same way this insoluble proteid of the gluten dissolves to some extent in hot dilute alcohol and separates on cooling. Such changes in solubility do not necessarily imply a "chemical" change, in the sense in which that term is usually employed, but are probably due to what perhaps ought to be more properly designated as a physical change.   It is probable that with many proteid substances solution depends on the formation of hydrates which are soluble in the solvent employed, as, for instance, zein, the principal proteid of maize, is wholly insoluble in water and also in absolute alcohol, but if water be present, solution in alcohol at once takes place, the amount of zein dissolved depending, within certain limits, on the quantity of water present.

It is the writer's opinion that the gluten is made up of two forms of the same proteid, one being soluble in cold dilute alcohol and the other not soluble.

The Amount of the Various Proteids contained in the Kernel of Wheat.

1000 grams of fine meal obtained by freshly grinding the entire kernel of spring wheat, and a like quantity of similar flour from winter wheat, were each extracted with 4000 cc. of 10-per cent. sodium-chloride solution, and as much of the extract as possible obtained by filtration, 2500 cc. of the clear extract being obtained from the spring wheat flour and 2600 from the winter wheat flour. As 100 cc. of solution were used for every 25 grams of flour taken, the amount of extract obtained was approximately equal to that from 625 grams of spring wheat flour and 650 grams of

winter wheat flour. These extracts were then dialyzed until all the chlorides were removed, which required five days. The precipitated globulin was then filtered from each, washed with distilled water, alcohol, absolute alcohol, and ether, removed from the filter and dried at 110°. From the spring wheat extract 3.8398 grams were obtained, equal to 0.624 per cent. of the flour, and from the winter wheat 3.9265 grams, equal to 0.625 per cent.

The filtrates from the globulin were then heated to 65° in a water-bath, and after being held at this temperature for some time the coagulum was filtered off and washed with hot water, alcohol, and ether, removed from the paper and dried at 110°. From the spring wheat 1.9714 grams were obtained, being 0.315 per cent. of the flour, and from the winter wheat 1.9614 grams, equal to 0.302 per cent.

The solutions filtered from each of these coagula were next heated just to boiling and the resulting coagulum filtered off, washed thoroughly, and treated as the preceding preparations had been. The spring wheat extract thus yielded 0.4743 gram, equal to 0.076 per cent.; the winter wheat extract 0.3680 gram, equal to 0.057 per cent.

The two extracts were next concentrated by boiling down over a lamp. They remained clear at first, but when somewhat concentrated, the proteid began to separate as a skin on the surface of the solution. When reduced to about one-fourth its original volume the coagulum was filtered off, washed with boiling water, alcohol, and ether, and dried at 110°. The spring wheat thus yielded 0.8737 gram, equal to 0.139 per cent.; the winter wheat 0.8721 gram, equal to 0.134 per cent. The filtrates from these two preparations were evaporated very nearly to dryness on water-baths. On cooling, much substance separated which, when treated with hot water, dissolved again. The insoluble coagulum was filtered from each, washed and dried in the usual manner. The spring wheat gave 0.8149 gram of substance, being 0.130 per cent. of the flour; the winter wheat 0.5795 gram, being 0.089 per cent. The total amount of proteid coagulating on concentration was therefore 0.269 per cent. for the spring wheat and 0.223 per cent. for the winter wheat.

The filtrates from these second coagula were then again evaporated to a syrup, and as no more insoluble matter separated they were each precipitated by pouring into strong alcohol. Large

precipitates resulted in each case, which, after settling and decantation of the alcohol, were dissolved again in a little water and reprecipitated by pouring into strong alcohol. Much coloring matter and sugar was held in solution, as proved by evaporation of the alcoholic mother-liquors. The precipitates were then thoroughly dehydrated with absolute alcohol, washed with ether and dried at 110°. The spring wheat extract thus yielded 6.9289 grams of substance; the winter wheat, 8.7517 grams. As these preparations were unquestionably very impure, and no practicable method of purification existed which could be carried out without great loss of substance, the nitrogen in each was determined and the proteid calculated by multiplying the result obtained by 6.25. The spring wheat preparation was thus found to contain 3.07 per cent. of nitrogen, equal to 19.19 per cent. of proteid, and the winter wheat preparation 5.15 per cent. nitrogen, equivalent to 32.18 per cent.

The amount of proteose and peptone thus found in the extract from the spring wheat was 1.3297 grams, which equals 0.213 per cent. of the flour, and in the winter wheat extract 2.8063 grams, equal to 0.432 per cent. of the flour.

We thus had in the sodium-chloride solution the following amounts of proteid :

	Spring Wheat.	Winter Wheat.
Globulin	0.624 per cent.	0.625 per cent.
Albumin	0.391	0.359
Coagulum	0.269	0.223
Proteose	0.213	0.432
Total	1.497	1.639

The remainder of the proteid matter of the seed forms the gluten. The proportion of gliadin and glutenin in this gluten was determined in the following manner :

200 grams of spring wheat flour, made from the entire seed, and a like quantity of a similar winter wheat flour, were each made into a dough and thoroughly washed with water as long as starch was removed. The gluten thus obtained, after freeing from loosely adhering moisture, was weighed and exactly one-half dried at 110° to constant weight. The spring wheat was thus found to yield 12.685 per cent. dry gluten, the winter wheat flour 11.858 per cent.

The other half of the gluten was cut up very fine and extracted as thoroughly as possible with alcohol of 0.90 sp. gr. The alcoholic extract was then evaporated to small volume, cooled, and the solution decanted from the precipitated proteid. This precipitate was then extracted with ether and dried at 110°. From the spring wheat gluten 4.3379 per cent. was obtained, and from the winter wheat 4.2454 per cent.

The residue extracted with alcohol was then dried at 110° and weighed. The spring wheat gluten contained 7.80 per cent. insoluble in alcohol, the winter wheat 7.504 per cent. reckoned on the wheat. Nitrogen was then determined in these residues dried at 110°, as well as in the dried gluten and also in the original flours. The washings of the glutens were collected in jars and allowed to settle; the sediments washed with water and with very strong alcohol and dried and weighed. The nitrogen in each was then determined. The results of these determinations and deductions drawn from them are given in the following table :

	Spring.	Winter.
Total nitrogen in the flour	1.950 per cent.	1.940 per cent.
Total gluten in the flour	12.685	11.858
Part of gluten insol. in alcohol	7.800	7.504
Per cent. of nitrogen in gluten	12.010	12.000
Total nitrogen in gluten in per cent. of flour	1.5222	1.4230
Total N in residue of gluten insoluble in alcohol	0.8245	0.7346
Total N extracted by alcohol	0.6977	0.6884
Gliadin (N × 5.68, assuming 17.60 per cent. N in gliadin	3.9630	3.9100
Gliadin by direct weighing	4.3379	4.2454
N in sediment from washing gluten	0.2239	0.1552

	Spring Wheat.		Winter Wheat.	
	N.	Proteid.	N.	Proteid.
Glutenin	0.8245 × 5.68 =	4.683	0.7346 × 5.68 =	4.173
Gliadin	0.6977 × 5.68 =	3.963	0.6884 × 5.68 =	3.910
Globulin	0.1148 =	0.624	0.1148 =	0.625
Albumin	0.0657 =	0.391	0.0603 =	0.359
Coagulum	0.0453 =	0.269	0.0379 =	0.223
Proteose	0.0341 =	0.213	0.0791 =	0.432
From H₂O washings of gluten	0.2239 × 5.68 =	1.272	0.1552 × 5.68 =	0.881
Total	2.0050	11.415	1.8703	10.603
Flour	2.10 × 5.68	11.93	1.94 × 5.68	10.96

VII.—The Formation of Gluten.

Wheat, so far as known, is the only plant whose seeds contain proteid matter separable in a coherent form from the other constituents by washing with water. When ground fine and mixed with a suitable quantity of water it yields a dough from which a light, porous bread can be made. The importance of this fact in bread-making is so great that considerable attention has been paid to gluten by the chemists who have studied wheat proteids.

The investigations of Günsberg, Martin, and of the writers, disprove the existence of gluten fibrin and mucedin, which are currently stated to exist in gluten, and demonstrate that, as Taddei maintained, gluten consists of two proteids only.

We have already referred, page 415, to the statements of Weyl and Bischoff that the proteid matter of the wheat kernel is *chiefly* a globulin substance, and that in contact with water it undergoes a change, presumably through the influence of a ferment by which gluten results.

If we examine the statements of these investigators we will find no evidence to support their view. They say: "On investigating the proteids of wheat meal, one of us found principally a globulin substance, which he designated, in consequence of its similarity to myosin of the muscle, vegetable myosin. This vegetable myosin must be the mother-substance of the gluten, since in the wheat meal, together with it, other proteids, if at all, exist only in very small amount." What the reasons were for concluding that the "myosin" formed nearly if not all the proteid of the wheat kernel does not appear. In view of the results obtained by the writers, this statement is certainly erroneous. Direct treatment of the meal with alcohol yielded extracts containing gliadin in exactly the same amount as obtained from the gluten made from an equal quantity of flour, and extraction of either flour or gluten with alcohol, after complete exhaustion with sodium chloride solution, also gave the same proportion of gliadin. This substance must therefore have existed in the seed, having the same composition and properties as in the gluten, and as it forms one-half of the gluten, it leaves the other half only as possibly derived from a globulin body through the influence of a ferment. If Weyl and Bischoff's view were correct, treatment of the flour with 10-per cent. salt solution ought to alter the character and quantity

of the gluten obtained, if not altogether to prevent its formation. This is not so, for the usual amount of gluten can readily be obtained from flour made into dough with 10-per cent. sodium-chloride solution and then washed with the same until starch is removed.

Weyl and Bischoff next state that, "with the aid of a 15-per cent. rock-salt solution the flour was extracted until no proteid could be detected in the extract; the residue of the meal kneaded with water then gave no gluten. *If the globulin substance is extracted no formation of gluten takes place.*" We have found that this is true if the flour is stirred up with a large quantity of salt solution, extracted repeatedly with fresh quantities of the same solution until no more proteid is dissolved, and the excess of solution removed by allowing the residue to drain on a filter as completely as possible. If, however, wheat flour is mixed at first with just sufficient salt solution to make a firm dough, this dough may then be washed indefinitely with salt solution, and will yield gluten as well and as much as if washed with water alone. This difference is due to the fact that when large quantities of salt solution are applied at once the flour fails to unite to a coherent mass and cannot afterwards be brought together, as is possible when treated with smaller quantities of solution.

Weyl and Bischoff then compare the formation of gluten to that of blood fibrin from fibrinogen under the influence of a ferment. They say that the formation of gluten is affected by all the conditions which interfere with the activity of ferments in general. " Large amounts of salt hinder the formation of gluten. Sulphates of magnesium and sodium behave like common salt." These statements are explained by what has been said above.

They then tried unsuccessfully to obtain the ferment in the following manner :

" We allowed meal with an equal weight of 90-per cent. alcohol to stand in closed vessels different lengths of time (in one case four months, then several times 3 to 4 weeks, frequently only 8 to 10 days). The vessels were repeatedly shaken and the yellow-colored alcoholic extract was poured off. The residue was freed from alcohol by pressing and evaporating at the ordinary temperature. After it was stirred up with water, little or no gluten was obtained. Evidently the globulin substance had been coagulated for the most part by the alcohol." It is clear that if the flour

were thus treated, the greater part of the gliadin would be removed. The writer has found that if flour is extracted with dilute alcohol until the gliadin is removed, and the residue freed from alcohol by exposure to the air, the latter will then yield no gluten when treated with water.

Sidney Martin next advanced a somewhat similar theory of the formation of gluten from the proteids contained in the seed. He states that alcohol extracts from gluten but one proteid substance ; that this is soluble in hot water but not in cold, and he therefore calls it an insoluble phytalbumose.

The residue of the gluten not dissolved by alcohol is uncoagulated proteid, if the alcohol has not been allowed to act too long. This substance he names gluten fibrin. Martin further says that gluten dissolves almost completely in $\frac{2}{10}$-per cent. hydrochloric acid, or $\frac{2}{10}$-per cent. potash solution, leaving a small residue of fat. The solution gives a copious precipitate when neutralized, but the supernatant liquid still contains a quantity of proteid which is the dissolved insoluble albumose. The whole of the gluten fibrin is reprecipitated by neutralization, that is, it is wholly converted into an albuminate.

Martin then asks : " Does flour contain gluten fibrin ? Does it contain insoluble phytalbumose ?" The first question he says cannot be answered directly. " The second is answered by extracting flour with 76–80 per cent. alcohol. This ought to contain the insoluble albumose if it were present as such in the flour, *but it does not contain it ;* it extracts only fat." This statement is certainly erroneous, for the writer has never failed in many experiments thus to extract this substance (gliadin) from the flour, and that too in the same amount and of the same properties and composition as from the gluten.

Martin concludes that insoluble albumose is not present as such in the flour. He then says : " Before proceeding to mention its precursor, it will be well to state that 10-per cent. sodium-chloride solution extracts from flour a large quantity of globulin and of albumose. This globulin is of the myosin type, coagulating between 55° and 60° C., and precipitated by saturation with sodium chloride and ammonium sulphate. Both the globulin and albumose are present in a much smaller quantity in the watery extract of the flour." From this it is evident that Martin has fallen into the same error as Weyl and Bischoff, mistaking the albumin for a myosin-like globulin, and being greatly misled as to its amount.

Continuing, Martin says: " The direction of the evidence is to show that the insoluble albumose is formed from the soluble. Moreover, I think that the globulin is transformed into the gluten fibrin, for I have been able to obtain from the globulin in solution a body having the same reactions as the gluten fibrin." What this evidence is which by its direction shows that the insoluble albumose is derived from the soluble, is not clear, and Martin makes no further statements on this point. That a body should be obtained from the solution containing the globulin which had the same reactions as the "gluten fibrin" is not surprising, for the so-called "albuminates" derived from nearly all globulins have no characteristic reactions, being merely soluble in dilute acids and alkalies, and precipitated by neutralization in the same way as "gluten fibrin." Martin then states his theory of the formation of gluten in the following scheme :

$$\text{Gluten} = \begin{cases} \text{Gluten fibrin} & \text{—precursor, globulin.} \\ \text{Insoluble albumose—} & \text{"} \quad \text{soluble albumose.} \end{cases}$$

This cannot be a correct representation of the formation of gluten, for it has been shown to be founded on two erroneous observations: first, that alcohol does not extract proteid matter from the flour when applied directly, and second, that at least one-half the proteid matter of the seed is a myosin-like globulin.

The results obtained by the authors and described in this paper have led to the conclusion that no ferment-action is involved in the formation of gluten; that but two proteid substances are contained in the gluten, glutenin and gliadin, and that these exist in the wheat kernel in the same form as in the gluten, except that in the latter they are combined with water in an amount equal to about twice the weight of the dried proteid. The reasons for this opinion are, first, that alcohol extracts the same gliadin in the same amount, whether applied directly to the flour, to the gluten, or to the flour previously extracted with 10-per cent. sodium-chloride solution; second, that $\frac{2}{10}$-per cent. potash extracts glutenin of uniform composition and properties from flour which has been extracted with alcohol or with 10-per cent. sodium-chloride brine and then with alcohol, as it extracts from gluten which has been exhausted with alcohol. Both glutenin and gliadin are necessary for the formation of gluten, as shown by the following experiments.

A portion of flour was washed completely free from gliadin by means of alcohol of 0.90 sp. gr., next with stronger alcohol, finally

with absolute alcohol, and air-dried. The residue was then rubbed up fine until all lumps were removed, and water carefully added and a dough made of the mass. A tolerably coherent dough was thus obtained, but much less elastic and tough than that produced from the untreated flour. This dough was then washed with water on a sieve, using every precaution to obtain a gluten, but none was formed. In another experiment 7.5 grams of very finely ground air-dried gliadin were mixed intimately with 70 grams of fine corn-starch and distilled water added. A plastic dough was thus produced, but it had no toughness. On adding a little 10-per cent. sodium-chloride solution, the dough became at once tough and elastic. This was then washed with great care on a sieve with cold water, a little 10-per cent. salt solution being added from time to time, but in spite of every precaution no gluten was obtained. The following experiment shows that the gliadin used was capable of forming gluten when glutenin was present, and also that salts have a marked influence on the toughness of resulting dough.

Two portions of flour weighing 100 grams each were taken, and after adding 5 grams of gliadin to one, both were made into dough with the same quantity of water. The two doughs presented marked differences; that to which the gliadin had been added was much tougher and more yellow than the other. They were then washed with water as long as starch separated. The gluten was dried superficially by wiping with a cloth and weighed in the moist state. That from 100 grams of flour to which 5 grams of gliadin had been added weighed 44.55 grams; that from 100 grams of flour alone weighed 27.65 grams. The moist glutens were dried at 110° to constant weight, and both yielded the same proportion of dry gluten, *viz.*, 34.6 per cent. The yield of dry gluten was accordingly, in the first case 15.41 grams, and in the second 9.56 grams. The difference, 5.85 grams, shows that the added gliadin was fully recovered in the gluten.

The figures show that these proteids combine with about twice their weight of water in forming gluten. The fact that the added gliadin entered so readily and completely into the formation of gluten indicates that it exists in the seed as such and undergoes no chemical change during extraction and drying.

The properties observed in testing the separated gliadin show how it acts in forming gluten, and explain many of the points observed by others and attributed to a ferment-action.

When treated with distilled water in small amount the fine ground air-dry gliadin at once forms a sticky mass which, on adding more distilled water, dissolves to a turbid solution. If, however, a very little sodium chloride is added to distilled water and this applied to gliadin that has been first moistened with pure water, a very coherent, viscid mass results which adheres to everything it touches and can be drawn out into long threads. If the gliadin is moistened with 10-per cent. sodium-chloride solution and then treated with a larger quantity of this solution, the substance unites to a plastic mass which can be drawn out into sheets and strings, but is not adhesive. From this it is evident why Ritthausen, in washing flours which gave a fluid gluten obtainable only in small quantity and with great difficulty, found that the addition of calcium sulphate to the wash-water rendered the gluten much more coherent and easily obtainable. The gliadin is thus proved to be the binding material which causes the particles of flour to adhere to one another, thus forming a dough. But the gliadin alone is not sufficient to form gluten, for it yields a soft and fluid mass which breaks up entirely on washing with water. The insoluble glutenin is probably essential by affording a nucleus to which the gliadin adheres and from which it is not mechanically carried away by the wash-water.

It might be supposed that this insoluble glutenin which so nearly resembles gliadin in composition results from an alteration of the latter brought about by the action of the mineral or other constituents of the seed or of the water. This is not probable, for the same amount of gliadin is extracted from flour directly by treating it with alcohol of 0.90 sp. gr. as is obtained from the gluten itself, and also the same amount is obtained after extracting the flour completely with 10-per cent. sodium-chloride solution and then with alcohol. The behavior of the gliadin towards 10-per cent. sodium-chloride solution shows why no gluten was obtained by Weyl and Bischoff from flour extracted with this solvent. The gliadin had under these conditions no adhesive qualities and therefore was unable to bind the flour into a coherent mass. If, however, the salt solution is added in small quantities and the flour kneaded and pressed, the particles are brought together and then adhere tenaciously.

VIII.—SUMMARY.

The proteids contained in the wheat kernel are:

I.—A *globulin* belonging to the class of vegetable vitellins, soluble in saline solutions, precipitated therefrom by dilution and also by saturation with magnesium sulphate or ammonium sulphate, but not by saturation with sodium chloride. Partly precipitated by boiling, but not coagulated at temperatures below 100°. The wheat kernel contains between 0.6 and 0.7 per cent. of this globulin. When dried at 110° its composition was found to be as follows:

<div align="center">

Wheat Globulin.

Carbon	51.03
Hydrogen	6.85
Nitrogen	18.39
Sulphur	0.69
Oxygen	23.04
	100.00

</div>

II.—An *albumin*, coagulating at 52°, which differs from animal albumin in being precipitated on saturating its solutions with sodium chloride or with magnesium sulphate, but not precipitated on completely removing salts by dialysis in distilled water. It was found to form between 0.3 and 0.4 per cent. of the wheat kernel, and to have the following composition when separated from solution in the coagulated form by heating to 60° C.:

<div align="center">

Wheat Albumin.

Carbon	53.02
Hydrogen	6.84
Nitrogen	16.80
Sulphur	1.2S
Oxygen	22.06
	100.00

</div>

III.—A *proteose*, precipitated (after removing the globulin by dialysis, and the albumin by coagulation) by saturating the solution with sodium chloride, or by adding 20 per cent. of sodium chloride and acidifying with acetic acid. This body was not analyzed in its unaltered form. On concentrating its solutions by boiling, a coagulum was gradually developed which formed about 0.3 per cent. of the wheat kernel and had the following composition:

Coagulum.

Carbon	51.86
Hydrogen	6.82
Nitrogen	17.32
Sulphur ⎱ Oxygen ⎰	24.00
	100.00

The solution filtered from the substance just described still contained a proteose-like body which was not obtainable in a pure state. Its amount could only be roughly estimated by precipitating the concentrated filtrate from the preceding substance with alcohol, and multiplying the nitrogen contained in the precipitate by 6.25. The amount of this proteose was from 0.2 to 0.4 per cent. of the seed. Both these substances are unquestionably derivatives of some other proteid in the seed, presumably the proteose first mentioned.

IV.— *Gliadin*, soluble in dilute alcohol and forming about 4.25 per cent. of the seed. It has the following composition :

Gliadin.

Carbon	52.72
Hydrogen	6.86
Nitrogen	17.66
Sulphur	1.14
Oxygen	21.62
	100.00

This is the proteid called gliadin by Taddei and plant gelatin by Dumas and Cahours. Mixed with impurities or altered to a greater or less extent by the process of separation, it has been described by Ritthausen under the name of gluten fibrin, plant gelatin, or gliadin, and mucedin, and by Martin has been termed insoluble phytalbumose. The mucin of Berzelius and of De Saussure were impure preparations consisting chiefly of this proteid. It is soluble in distilled water to opalescent solutions which are precipitated by adding a little sodium chloride. It is completely insoluble in absolute alcohol, but slightly soluble in 90-per cent. alcohol, and very soluble in 70- to 80-per cent. alcohol, and is precipitated from these solutions on adding either much water or strong alcohol, especially in the presence of much salts; soluble in very dilute acids and alkalies, and precipitated from these solutions by neutral-

ization, unchanged in properties and composition. This proteid is one on which the formation of gluten largely depends.

V.—*Glutenin*, a proteid insoluble in water, saline solutions and dilute alcohol which forms the remainder of the proteids of the wheat kernel, generally about 4 to 4.5 per cent. of the seed. This substance is soluble in dilute acids and alkalies and is precipitated from such solutions by neutralization. Dissolved in $\frac{2}{10}$-per cent. potash water, precipitated by neutralization and, after thorough extraction with alcohol and ether, again dissolved in potash water, the solution filtered *clear*, precipitated by neutralization and dried at 110°, it has the following composition:

Glutenin.

Carbon	52.34
Hydrogen	6.83
Nitrogen	17.49
Sulphur	1.08
Oxygen	22.26
	100.00

Unless prepared as above described, the impurities are not removed and the analyses are discordant. This proteid was first described by Taddei under the name of zymom. Liebig as well as Dumas and Cahours named it plant fibrin. Ritthausen called it gluten casein, Weyl and Bischoff considered it to be an albuminate form of a myosin-like globulin. Martin named it gluten fibrin and likewise considered it to be an albuminate form of a myosin-like globulin.

VI.—Wheat gluten is composed of gliadin and glutenin. Both these proteids are necessary for its formation. The gliadin with water forms a sticky medium, which by the presence of salts is prevented from becoming wholly soluble. This medium binds together the particles of flour, rendering the dough and gluten tough and coherent. The glutenin imparts solidity to the gluten, evidently forming a nucleus to which the gliadin adheres and from which it is consequently not washed away by water. Gliadin and starch mixed in the proportion of 1 : 10 form a dough, but yield no gluten, the gliadin being washed away with the starch. The flour freed from gliadin gives no gluten, there being no binding material to hold the particles together so that they may be brought into a coherent mass.

Soluble salts are also necessary in forming gluten, as in distilled water gliadin is readily soluble. In water containing salts it forms a very viscid, semi-fluid mass, which has great power to bind together the particles of flour. The mineral constituents of the seeds are sufficient to accomplish this purpose, for gluten can be obtained by washing a dough with distilled water.

VI.—No ferment-action occurs in the formation of gluten, for its constituents are found in the flour having the same properties and composition as in the gluten, even under those conditions which would be supposed completely to remove antecedent proteids or to prevent ferment-action. All the phenomena which have been attributed to ferment-action are explained by the properties of the proteids themselves as they exist in the seed and in the gluten.

LABORATORY OF THE CONN. AGRIC. EXPERIMENT STATION, NEW HAVEN.

ON THE DECOMPOSITION OF THE SALTS OF MONO-CHLORACETIC AND MONOBROMACETIC ACIDS.

BY J. H. KASTLE AND B. C. KEISER.

The interesting results obtained in the study of the decomposition of silver chloracetate in aqueous solution[1] led us to undertake a rather more exhaustive study of the decomposition of other salts of this and similarly constituted acids, especially of the salts of those metals whose chlorides and bromides are freely soluble in water, in the hope of being able to arrive at a more complete solution of the problem presented by such decompositions. In the following pages are given the results of this investigation up to the present time, together with such discussion of the hypothesis originally offered by one of us in explanation of the decomposition of silver chloracetate as these fresh data would seem to warrant.

[1] This Journal **14**, 586.

The Salts of Monochloracetic Acid.

Quite a number of the salts of monochloracetic acid have been prepared by different observers from time to time. The difficulties in the way of obtaining the most of these in anything like a desirable condition of purity will, however, doubtless warrant a brief description, together with an account of the method of preparation of those which have been used in this investigation, despite the fact that many of them, if not all, have already been described.

Anhydrous Potassium Chloracetate.—This salt is best prepared by treating the required amount of caustic potash dissolved in absolute alcohol, with an equivalent quantity of chloracetic acid dissolved in the same solvent. The solution of the acid is slowly added to the solution of caustic potash. The mixture is constantly stirred, and kept cool by immersing the vessel containing it in cracked ice. Under these conditions the anhydrous salt is precipitated in the form of a fine, white, crystalline precipitate. During the operation small portions of the mixture are tested from time to time with phenolphthaleïn, and when found to be entirely neutral the salt thus obtained is filtered off and dried as rapidly as possible on filter-paper. When dry the salt has a pearly luster, is soft and soapy to the touch, stable in dry air, and very soluble in water. On analysis it was found to yield numbers which agree fairly well with those demanded by the theory, and repeated determinations of the amount of chlorine in the condition of chloracetic acid and of that present as free chloride have shown it to contain 97–98 per cent. of pure potassium chloracetate.

Anhydrous Sodium Chloracetate.—The method employed to best advantage in the case of this salt is essentially the same as that given in the above for the preparation of the potassium salt. The salt thus obtained by adding an alcoholic solution of monochloracetic acid to one of caustic soda is anhydrous, pearly in luster, soapy to the touch, very soluble in water, and of about the same degree of purity as the potassium salt.

Anhydrous Ammonium Chloracetate.—This salt is best prepared by treating a saturated solution of ammonia in absolute alcohol with an alcoholic solution of the acid, adding the latter to the former gradually, and keeping the vessel containing the mixture immersed in cracked ice. The pure, anhydrous ammonium

salt separates out under these conditions in the form of beautiful, delicate, white needles.

Magnesium Chloracetate, $(CH_2ClCOO)_2Mg + 2H_2O$. — This salt was made by treating the oxide of magnesium with a concentrated aqueous solution of the acid and evaporating under a bell-jar in a current of dry air. The salt is exceedingly soluble both in alcohol and water. The following numbers were obtained on analysis:

	Found.	Calculated.
Mg	9.76	9.71 per cent.

Calcium Chloracetate, $(CH_2ClCOO)_2.Ca + H_2O$. — This salt was obtained by neutralizing an aqueous solution of the acid with pure, precipitated calcium carbonate and evaporating the solution under a bell-glass in a current of dry air. Like the magnesium salt it is exceedingly soluble in water and also in alcohol. It crystallizes in fine, white needles. On analysis it gave the following numbers:

	Found.	Calculated.
Ca	16.36	16.32 per cent.

Anhydrous Strontium Salt.—The strontium salt was prepared by dissolving the carbonate in an aqueous solution of the acid by the aid of heat, filtering, and adding about an equal volume of alcohol. Under these conditions the salt comes down in the form of a beautiful, white, crystalline precipitate. Of all the salts of monochloracetic acid, it and the barium salt are probably the easiest to obtain in good yield and in a condition of purity. On analysis the following numbers were obtained:

	Found.	Calculated.
Sr	31.74	31.87 per cent.

The barium and lead salts were also prepared by well known methods which need no particular description. It may be said, however, in this connection that the barium and strontium salts would be, in consequence of their purity and the ease with which they may be prepared, excellent material for such an investigation as this, were it not for the fact that they are just a little too insoluble in very small quantities of water.

The Rate of Decomposition of Potassium Chloracetate.

At ordinary temperatures, ranging from 20°–25° C., the decomposition of the potassium salt in water into potassium chloride and

glycollic acid is a very slow one, as is shown by the following experiments:

Time, 94 days; quantity of salt in each case, 0.1325 gram.

	I.	II.	III.
Water	0.9 cc.	2.7 cc.	9 cc.
Percentage decomposed	5	2.5	1.75

When heated with water, however, the decomposition proceeds —in some instances at any rate—with great rapidity, as indicated in the following table:

TABLE I.—*Showing the Effect of Water on the Decomposition of Potassium Chloracetate.*

Time, 2 hours; temperature, 100° C.; quantity of salt in each experiment, 0.1325 gram.

No. of Experiment.	Quantity of Water in cc.	Percentage Decomposed.
1	0.09	75 : 74
2	0.18	68 : 68.5
3	0.27	60 : 59.5
4	0.36	55 : 51
5	0.45	47.5 : 47
6	0.54	43 5 : 43
7	0.63	39.5 : 39.5
8	0.72	36 : ...
9	0.81	34 : 34
10	0.9	32 : 32
11	1.8	22 : 23 : 22
12	2.7	... : ...
13	5.4	... : ...
14	9	14.5 : 14
15	27	8.5 : ...
16	90	9.5 : ...
17	180	9.5 : 9
18	270	11 : 10.5
19	360	11.5 : 11.5
20	450	12 : 12.5
21	540	13.5 : ...
22	1080	8.5 : 9

Two methods of course suggest themselves for measuring the amount of this decomposition. Either the quantity of free chloride

may be determined by means of standard solutions of silver nitrate and ammonium sulphocyanide, or the glycollic acid formed as a result of the decomposition may be measured directly by means of standard alkali. The results given in Table I above were obtained by the latter method, using a $\frac{1}{10}$-normal solution of caustic potash, with phenolphthaleïn as the indicator.

With the smaller quantities of water, from 0.09 cc. to 1.8 cc., the experiments were tried in sealed glass tubes about 75 mm. long and of 8 mm. inside diameter. The experiments requiring larger amounts of water were tried either in tubes or flasks connected with small inverted condensers. The pressure produced in the sealed tubes with the smaller quantities of water seems to exert no influence upon the speed of the reaction. Of the several numbers obtained in the case of Exp. 11, Table I, two, 22 and 23 per cent., were obtained working in the open tube with inverted condenser, and one, 22 per cent., in the sealed tube.

It will be seen in the above table that the results obtained in the decomposition of potassium chloracetate agree fairly well among themselves, especially when the small quantities both of salt and water are considered, and also that every drop of a $\frac{1}{10}$-normal solution corresponds to about 0.5 per cent.

It is, however, to be remarked in this connection that these results were obtained from the same batch of potassium chloracetate, and that a comparison of the results obtained from different batches of the salt shows a greater variation for corresponding states of dilution. This variation shows itself in those experiments only in which the smaller quantities of water have been employed, *viz.*, from 0.09 cc. to 1 cc.; and even here where it is found to be the greatest, the same relative values are found to hold for the decomposition at corresponding states of dilution. The variation is doubtless to be attributed to the fact that it is practically impossible to obtain any two batches of salt of exactly the same grade of purity. It is to be concluded from these experiments that the decomposition of potassium chloracetate in water, like that observed for the corresponding silver salt, suffers a gradual retardation with increasing quantities of the solvent.

The Rate of Decomposition of Sodium Chloracetate.

TABLE II.—*Showing the Effect of Water on the Decomposition of Sodium Chloracetate.*

Time, 2 hours; temperature, 100° C.; quantity of salt in each experiment, 0.1165 gram.

No. of Experiment.	Quantity of Water in cc.	Percentage Decomposed.
1	0.09	65 : 64
2	0.18	57.5 : 57.5
3	0.27	50.5 : 50.5
4	0.36	45.5 : ...
5	0.45	39 : ...
6	0.54	34.5 : 35.5
7	0.63	32.5 : 32.5
8	0.72	30 : ...
9	0.81	28 : 28
10	0.9	26 : 26.5
11	1.8	18 : 18.5
12	9	11 : 10.5
13	90	7.5 : 6.5
14	180	7.5 : 7
15	270	10 : 10
16	360	10 : 10.5
17	450	10 : 10
18	540	11.5 : 12.5
19	1080	8

The results set forth in Table II require no special comment. What has already been observed in the case of those obtained with the potassium salt applies with equal force to these. They very clearly show the retarding influence of water upon the course of the reaction. It is worthy of note, however, in this connection, that the results obtained both with sodium and potassium salts would seem to indicate that the retarding effect of the water reaches a maximum at some dilution between 90 cc. and 1 litre, the exact point not having been determined, and that consequently the rate of decomposition becomes practically constant. The slight variations which are experienced in passing through the several stages of greater dilution are probably to be accounted for partly by reason of the fact that it was found more difficult to control the temperature where such large quantities of water were employed, and partly by reason of the difficulty of getting a sharp end-reaction with the indicator in these conditions of greater dilution.

The Effect of Time upon the Decomposition of Potassium Chloracetate.

In discussing the results obtained in the study of the decomposition of silver chloracetate it was stated that the decomposition in question was a simple, non-reversible reaction, unattended by the formation of secondary products of any kind. So far as we have been able to discover, the same applies to the decomposition of all the salts of this acid thus far studied, and in this connection it may not be out of place to cite the fact that such attempts as have been made on the part of other observers to prepare chloracetic acid from hydrochloric acid and glycollic acid have given only negative results.

In order finally to settle upon the nature of the chemical process here involved, it was thought desirable to determine not only the effect of varying amounts of water upon the course of the reaction, but also the effect of time. This was done with the following results:

TABLE III.—*Showing the Effect of Time upon the Decomposition of Potassium Chloracetate.*

Temperature, 100° C.; quantity of salt in each experiment, 0.1325; quantity of water, 2.7 cc.; $a =$ 100 per cent.

No. of Experiment.	Time $= T$.	Percentage Decomposed $= x$.	K.
1	60 minutes	8 : 7.5	.0015
2	120 "	15 : 15	.0014
3	180 "	23 : 22	.0014
4	240 "	31 : 31.5	.0015
5	300 "	36 : 37	.0015
6	360 "	40 : 39.5	.0014
7	420 "	44	.0014
8	480 "	47 : ...	.0013
9	540 "	49 : 50	.0013
10	600 "	54.5 : 55	.0013

It will be seen from these results that the decomposition here studied obeys, for the given dilution, the law for simple decompositions as first established by Wilhelmy for the inversion of cane-sugar, and satisfies the mathematical formula for the same:

$$\log \frac{a}{a - x} = KT \cdot 4343.$$

We may also conclude that in the chemical process here being studied we have but one substance affected.

The Decomposition of the Salts of Monochloracetic Acid in Water is independent of the Nature of the Base.

In view of the hypothesis put forward concerning the decomposition of silver chloracetate it became of interest to determine the extent of the decomposition for the various salts of chloracetic acid at the same or corresponding states of dilution. Such salts as have been described above were employed in these experiments for which the following conditions were observed:

Time $=$ 2 hrs.   Temperature $=$ 100° C.

Quantities of water: in Series No. I, 0.9 cc. for the salts of univalent metals, and 1.8 cc. for those of bivalent metals; in Series No. II, 2.7 cc. for the salts of univalent metals, and 5.4 cc. for the salts of bivalent metals; in Series No. III, 9 cc. for the salts of univalent metals, and 18 cc. for those of bivalent metals.

Quantity of each of the several salts: the thousandth part of one molecular weight in grams.

The results obtained in these experiments are given below in Table IV.

TABLE IV.—*Showing the Decomposition of several of the Salts of Monochloracetic Acid under the Same Conditions.*

	I.	II.	III.
Potassium Salt	32. per cent.	15. per cent.	10.7 per cent.
Sodium Salt	25.5	16.	10.75
Ammonium Salt	27.	16.25	10.5
Magnesium Salt	24.5	16.	...
Calcium Salt	26.5	15.75	11.75
Strontium Salt	25.5	15.	11.
Barium Salt	26.7	15.25	10.7
Lead Salt	...[1]	...[1]	10.

These results clearly indicate that the decomposition here taking place is independent of the nature of the base. This of course does not hold for those salts the metals of which yield insoluble chlorides, such as silver, mercury in the mercurous condition, etc.

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[1] At these dilutions the lead salt was not completely soluble and hence was not determined.

The Velocity of Decomposition of Potassium Chloracetate at Normal, ⅓-Normal, and $\frac{1}{10}$-Normal States of Dilution.

In order to be able to compare more accurately the velocity of decomposition with the coefficients of affinity of hydrochloric and monochloracetic acids respectively, the endeavor has been to determine the coefficients of the velocity of the decomposition at *normal, ⅓-normal* and $\frac{1}{10}$-*normal* states of dilution. These particular states of dilution having been selected for the reason that the coefficients of affinity of the two acids mentioned have been accurately determined under these conditions.

In consequence of the constant removal of some of the salt from the solution by virtue of its decomposition, no particular state of dilution can be preserved for a sufficient length of time to enable the determination to be made directly. To meet this difficulty the following method was resorted to, which, together with the results obtained, is given below :

No. of Experiment.	Quantity of Salt.	Quantity of Water in cc.	Time in Minutes.	Percentage decomposed.	K.
1	0.1325 gram	0.53	135	45.	0.0044
2	"	"	150	49.5	0.0045
3	"	"	165	52.	0.0044
4	"	"	180	55.	0.0044
5	"	1.03	240	47.	0.0026
6	"	"	255	48.	0.0026
7	"	"	285	51.5	0.0026

The several values of K are obtained from the data given in the columns marked "Time" and "Percentage decomposed," by means of the formula $\log \dfrac{a}{a-x} = KT.4343$, to which attention has already been called (see p. 477).

This coefficient of the velocity of the decomposition in passing from twice-normal to normal is thus found to be 0.0044 ; while that obtained in passing from normal to ⅓-normal is found to be 0.0026. The mean therefore of these two values $\dfrac{0.0044 + 0.0026}{2} =$ 0.0035 must approximate very closely to the true coefficient of velocity for normal dilution. The extra 0.03 cc. of water over and above that required to form a twice-normal and normal solution of the amount of salt taken was added in these and certain other

experiments, for the reason that, while the potassium salt used was anhydrous, a modification of the potassium salt exists containing one and a half molecules of water of crystallization. Hence, in order to do away with any disturbing influence upon the proper dilution which the tendency on the part of the anhydrous salt to form such a hydrate might produce, it was deemed expedient at the time these experiments were tried, to add the extra 0.03 cc., this amount being the nearest measurable quantity to that required by the theory.

The following results furnish the necessary data for the determination of the coefficient of velocity at $\frac{1}{3}$-normal :

No. of Experiment.	Quantity of Salt taken.	Quantity of Water in cc.	Time in Minutes.	Percentage decomposed.	K.
1	0.1325 gram	2.28	180	25	0.001597
2	"	3.03	195	25	0.001474

Hence K for $\frac{1}{3}$-normal $= \dfrac{0.001597 + 0.001474}{2} = 0.001535.$

By the same method was the following number obtained for $\frac{1}{10}$-normal :

No. of Experiment.	Quantity of Salt taken.	Quantity of Water in cc.	Time in Minutes.	Percentage decomposed.	K.
1	0.1325 gram	9.03	105	8.5	...
2	"	"	120	9.5	0.00084
3	"	10.03	120	9.	...
4	"		135	10.	0.00078

Hence K for $\frac{1}{10}$-normal $= \dfrac{0.00084 + 0.00078}{2} = 0.00081.$

A comparison of these coefficients of velocity among themselves, and with the coefficients of affinity of monochloracetic acid at the same states of dilution, reveals in an interesting way the dependence of the velocity of this decomposition at these several states of dilution upon the relative strengths of the acids concerned in this reaction.

According to Ostwald, the several coefficients of affinity of monochloracetic acid, in terms of that of hydrochloric acid as unity, are for these dilutions as follows:

Coefficients of the Affinity of Monochloracetic Acid : HCl $= 1$.	Coefficients of the Velocity of the Decomposition of Potassium Chloracetate.
Normal $= 0.51$	Normal $= 0.0035$
$\frac{1}{3}$-Normal $= 0.07$	$\frac{1}{3}$-Normal $= 0.0015$
$\frac{1}{10}$-Normal $= 0.213$	$\frac{1}{10}$-Normal $= 0.0008$

For the sake of the comparison the coefficients of velocity have been placed by their side. It will be seen from these numbers that the affinity of monochloracetic acid in $\frac{1}{10}$-normal dilution is about *four* times as great as it is at normal. The coefficients of velocity in the other column show just as clearly that the rate of the decomposition at $\frac{1}{10}$-normal dilution is about *one-fourth* as great as it is at normal. In other words, the velocities of the decomposition of potassium chloracetate at normal and $\frac{1}{10}$-normal states of dilution are inversely proportional to the coefficients of affinity of monochloracetic acid at the same states of dilution.

$$\underset{\frac{1}{10}\text{-N.}}{0.213} : \underset{\text{N.}}{0.051} :: \underset{\text{N.}}{0.0035} : \underset{\frac{1}{10}\text{-N.}}{0.0008}$$

The equality of the two ratios is as close as could be expected, considering the fact that the two sets of numbers were arrived at by the study of altogether different chemical processes.

In the same way we have :

$$\underset{\frac{1}{3}\text{-N.}}{0.07} : \underset{\text{N.}}{0.051} :: \underset{\text{N.}}{0.0035} : \underset{\frac{1}{3}\text{-N.}}{0.0015}$$

Here the inverse proportionality does not hold as strictly as in the above. This may possibly be accounted for in this way : Ostwald's numbers for normal and $\frac{1}{3}$-normal, 0.051 and 0.07 respectively, were arrived at by different methods, and hence, as he himself says, are not strictly comparable. The numbers for normal and $\frac{1}{10}$-normal, *viz.*, 0.51 and 0.213, were, however, obtained by the same method, and here we find the agreement as close as could be desired.

The Effect of Glycollic Acid upon the Rate of the Decomposition.

In studying the decomposition of the silver salt of chloracetic acid it was found that the glycollic acid exerted a slight retarding influence upon the course of the reaction. Strange to say, however, the reverse of this has been found to be true in the case of the potassium salt. That is, the effect of the glycollic acid upon the decomposition is one of acceleration rather than retardation. At present this is very nearly all that may be said concerning the influence of this substance, for the reason that, while a great deal of time and attention has been given to this particular part of the subject, the results obtained as yet are by no means as satisfactory as could be desired. This is largely owing to the fact that the

influence exerted by this compound is at best but slight ; so slight, indeed, in some cases that, unless the decomposition be extraordinarily prolonged—which in some instances is impracticable—the acceleration is not accurately measurable by the means employed.

The following are some of the results obtained :

TABLE V.—*Showing the Effect of Glycollic Acid upon the Decomposition of Potassium Chloracetate.*

Temperature, 100° C.

No. of Experiment.	Potassium Salt taken.	Quantity of Water in cc.	Time in Hours.	Percentage Decomposed: Alone.	With .076 gram Glycollic Acid.
1	0.1325 gram	1	1	16 : 16.5	17.5 : 18
2	"	1	2	28 : 28.5	31 : 32
3	"	1	3	40.5 : 41	44 : 46.5
4	"	3	1	9 : ...	10 : ...
5	"	3	2	16 : ...	19 : ...
6	"	3	3	24.5 : ...	30 : ...
7	"	10	1	5 : ...	7 : ...
8	"	10	2	9 : ...	11 : ...
9	"	10	3	13.5 : ...	15 : ...

From these results it would appear that the slight acceleration produced by this substance is independent of the state of dilution. As illustrative of this compare the results of Exp. No. 1 with Nos. 5 and 9 ; also No. 2 with No. 6 and No. 4 with No. 8, in the above table. It would also appear from the results given in Table VI (below) that the acceleration is directly proportional to the quantity of glycollic acid present.

TABLE VI.

Time, 3 hours ; temperature, 100° C. ; quantity of salt in each case, 0.1325 gram ; quantity of water, 2.28 cc.

	I.	II.	III.	IV.
Quant. of glycollic acid	none	0.019 gr.	0.038 gr.	0.076 gr.
Perc. of decomposition	28.	29.25	30.5	33.25
Acceleration	...	1.25	2.5	5.25

In this connection it occurred to us to try the action of other acids upon the course of the decomposition. The effect of the

following has been tried with rather remarkable results: nitric, hydrochloric, sulphuric, formic, acetic, propionic, and malonic. It has been found that those weaker than monochloracetic *accelerate* the decomposition in the order of their strength—that is, formic accelerates it more than glycollic, and glycollic more than acetic, etc.; whereas, with those stronger than monochloracetic exactly the reverse seems to be true—that is, hydrochloric and nitric *retard* the decomposition very greatly and nearly to the same extent, and both more than sulphuric, etc.

The data now at hand are not sufficient to warrant any further statement as to the influence of acids in general upon the decomposition now being studied; much less do they permit of any speculation as to the bearing of all this upon the original problem. It is believed, however, that further study in this direction will yield results of considerable value and furnish one of the most interesting chapters in the complete solution of the problem now under investigation.

TABLE VII.—*Showing the Effect of Potassium Chloride upon the Decomposition of Potassium Chloracetate.*

Temperature, 100° C.; quantity of salt in each case, 0.1325 gram.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Quant. water in cc.	1	1	1	3	3	3	10	10
Time in hours	1	2	3	1	2	3	2	2
Perc. dec. (alone)	16.5	28	41	9	16	24.5	12	12
Perc. dec. with 0.0745 gram KCl	18	31	44.	9.5	16.5	28	13	12.5

The influence of potassium chloride has also been studied. About all that can be said at present is that it, like the glycollic acid, exerts a slight accelerating influence upon the decomposition, as may be seen from the results given in Table VII. It may be said in this connection that sodium bromacetate, by reason of its perfect purity and more ready decomposibility, has furnished a most excellent material with which to study the influence of both products of this reaction upon the decomposition. We hope in the near future to reach results better and more concordant than it has been found possible to obtain in this connection with potassium chloracetate.

Monobromacetic Acid.

This investigation, originally undertaken with the view to determine the relative velocities of decomposition of the silver salts of the several principal members of the series of haloid fatty acids, has so outgrown its original bounds, and so many points of interest have revealed themselves in connection with the best known of these acids—monochloracetic—as the work progressed, that while the original aim of the study has not been lost sight of, up to the present only one other acid, monobromacetic, has received attention.

Anhydrous Sodium Bromacetate.—This salt was prepared by slowly adding to a saturated aqueous solution of sodium carbonate the required quantity of the pure monobromacetic acid. The mixture was constantly stirred and its reaction tested from time to time. To the neutral solution thus obtained there was added, with constant agitation, a considerable quantity of absolute alcohol. Under these conditions the salt was obtained in the form of white, pearly leaflets of great purity. It may be dried in the usual manner upon filter-paper and finally under the desiccator. In appearance it strikingly resembles the salts of the corresponding chlor-acid. It is stable in dry air and freely soluble in cold water. Solutions of it were found to be perfectly neutral and to give no turbidity with silver nitrate. On analysis the following number was obtained for the sodium :

	Found.	Calculated for the Anhydrous Salt.
Na	14.43	14.32 per cent.

Decomposition of Sodium Bromacetate in Water.

In studying the decomposition of this salt a remarkably interesting observation was made. It was observed that when this salt was heated with small quantities of water a small quantity of a white, waxy substance resulted, which dissolved but slowly when treated with larger quantities of water, giving rise gradually, however, to an acid solution.

In order to determine the nature of this substance, about 8 grams of the sodium salt were heated for an hour and a half with about 5 cc. of water. The resulting mass was then treated with a considerable quantity of cold water to remove the sodium bromide and any other soluble products of the reaction; it was then filtered

and the white mass washed repeatedly with small amounts of cold water, dried and weighed. It was found to weigh 0.8 gram. The substance thus obtained was found to melt at 160° C.; when boiled with water it slowly dissolved; the solution became acid in reaction; and on cooling the substance partially separated out again in the form of a white powder, showing a great tendency to remain suspended in the liquid. It was found to dissolve very freely in strong ammonia, giving rise to an exceedingly soluble product.

It also dissolves in solutions of caustic potash and soda, and in order to determine its composition the larger portion of it was boiled for some time with water and the required amount of lime. The solution thus obtained was evaporated to small bulk, and while hot, filtered and set aside. After standing over night the calcium salt crystallized out in the form of white, satiny, needle-shaped crystals. These were filtered off, air-dried, and the calcium determined as the sulphate, with the following result:

	Found.	Calculated for $(CH_2OH.COO)_2Ca + 3H_2O$.
Ca	16.39	16.39 per cent.

This analysis and the mode of formation both indicate that the substance is glycollide. The fact that such a substance may be produced in such a decomposition, even in the presence of much more than the quantity of water necessary to form glycollic acid at once, is one of particular interest in this connection. It would seem to indicate that, in all such decompositions, the action of water, aside from promoting dissociation, is purely one of a secondary kind, and that, strictly speaking, such reactions are to be interpreted as taking place in two stages instead of one, as commonly represented, thus:

(1) $CH_2Br.COONa = NaBr + CH_2COO.$

(2) $CH_2COO + H_2O = CH_2OH.COOH.$
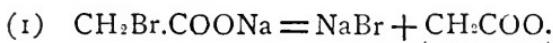
The decomposition of sodium bromacetate in water is an exceedingly rapid one. The effect of dilution upon the velocity of the decomposition is much the same as that already described at length for the salts of the chlor-acid. In the following table, No. VIII, are given the results thus far obtained. The several states of dilution at which these experiments have been tried were chosen with the view to determine the coefficients of velocity for normal, $\frac{1}{3}$-normal and $\frac{1}{10}$-normal solutions.

TABLE VIII.—*Showing the Effect of Water upon the Decomposition of Sodium Bromacetate.*

Temperature, 100° C.; quantity of salt in each case, 0.1610 gram.

No. of Exp.	Quan. of Water in cc.	Time in minutes.	Percentage decomposed.	K.	A.
1	0.5	8	51 : 52	.0916	$\dfrac{.0916 + .0513}{2} = .0714$ N.
2	1.	12	46 : 46	.0513	
3	1.5	20	54 : 54	.0388	$\dfrac{.0388 + .0269}{2} = .0328 \frac{1}{3}$-N.
4	3.	25	49 : 49	.0269	
5	5.	30	48 : 47.5	.0218	$\dfrac{.0218 + .0173}{2} = .0195 \frac{1}{10}$-N.
6	5.	300	99	...	
7	10.	40	50	.0173	

In column A of the table are given those mean values which represent the coefficients of velocity at normal, $\frac{1}{3}$-normal, and $\frac{1}{10}$-normal states of dilution. It is interesting to note in this connection that these several values stand in very much the same relation to each other that do those obtained for potassium chloracetate (see p. 481). Each of these values, however, is about twenty times greater than those obtained in the case of the potassium salt of the chlor-acid.

Thus we have:

Coefficients of Velocity for Potassium Chloracetate $\times$ 20.	Coefficients of Velocity for Sodium Bromacetate.
Normal $= .0035 \times 20 = .0700$	.0714
$\frac{1}{3}$-Normal $= .0015 \times 20 = .0300$	.0328
$\frac{1}{10}$-Normal $= .0008 \times 20 = .0160$	.0195

thereby showing that, while the salts of bromacetic acid are twenty times more unstable than those of chloracetic acid, their decomposition is nevertheless retarded by water by amounts proportionate to those observed for the decomposition of the salts of the chlor-acid.

It might be well in passing to call especial attention to experiments Nos. 5 and 6, Table VIII, as showing, first, that the decomposition can reach completion and, secondly (compare time and amounts decomposed in 5 and 6), that the time required for completion is ten times as long as that required for the decomposition of one-half of the substance.

For the reason that such large amounts of decomposition could be obtained with the sodium bromacetate in such comparatively

short intervals of time, it afforded an excellent material with which to determine the influence of glycollic acid upon the velocity of the reaction.

The following results have been obtained:

TABLE IX.—*Showing the Effect of Glycollic Acid upon the Decomposition of Sodium Bromacetate.*

Temperature, 100° C.; quantity of salt in each case, 0.1610 gram; quantity of glycollic acid, 0.076 gram.

No. of Exp.	Quantity of Water in cc.	Time in Minutes.	Percentage decomposed.	Percentage taken from Table VIII.	Acceleration.	
1	0.5	8	55.	51.5	3.5	
2	1.	12	54.	46.	8.	
3	1.5	20	61.	54.	7.	
4	3.	25	55.	49.	6.	Mean = 5.2
5	5.	30	51.5	47.5	4.	
6	10.	40	53.	50.	3.	
7	50.	60	60.	55.	5.	

These results strengthen the conclusion already reached concerning the influence of this acid upon the decomposition (see p. 482). The acid slowly accelerates the decomposition, and seems in its action to be independent of the dilution. It is true that the numbers here obtained for the several dilutions do not agree among themselves quite as well as might be expected. In only one case, however, is the departure from the mean value (5.2) greater than 2 ; there are just the same number of departures on one side as on the other, and it should also be borne in mind that in each case it was found necessary to weigh the acid, which, it will be remembered, is deliquescent and rather difficult to preserve of uniform composition. The fact that the acceleration here produced by the glycollic acid is so nearly the same for the different dilutions, and so nearly the same also for that observed in the case of the potassium chloracetate (compare Exp. 1 with those in Table VI), renders it unnecessary to apply any correction to the coefficients of velocity given above, for the reason that this correction would apply equally to each at the several dilutions and also to both sets alike. Each would become a trifle smaller, but the same relation would hold for those of each acid among themselves.

Summary and Conclusion.

The more salient features of the decomposition of the salts of monochloracetic and monobromacetic acids, as clearly indicated by the results given in detail above, are briefly these:

1. The decomposition is greatly retarded by increasing the · quantity of water, in which medium the decomposition readily takes place.

2. The decomposition is one of a simple, non-reversible kind, and may be carried to completion.

3. The decomposition, at certain states of dilution, probably at all, is independent of the nature of the base or metal in combination with the acid.

4. The coefficients of velocity of the decomposition at normal, $\frac{1}{2}$-normal and $\frac{1}{10}$-normal dilutions are inversely proportional to the coefficients of affinity of monochloracetic and monobromacetic acids at these several states of dilution.

5. The decomposition reaches a minimum at a dilution somewhat above $\frac{1}{10}$-normal (the exact point not yet determined), from which point on to a dilution of 1000 litres the decomposition is nearly constant.

6. The velocity of the decomposition is slightly accelerated by glycollic acid proportionately to the quantity of the acid present. Other acids weaker than monochloracetic have also been found to *accelerate* the decomposition in the order of their affinities. With acids stronger than monochloracetic exactly the reverse of this has been found to hold.

7. The velocity of the decomposition is also slightly accelerated by potassium chloride.

In discussing the results obtained in the case of the decomposition of silver chloracetate it was assumed by way of explanation that the salt dissociates in water, and that we have acting upon the metal, potentially at least, two acids or two acid ions, one of monochloracetic, the other of hydrochloric acid. The affinity of hydrochloric acid, in consequence of its extreme dissociation even in concentrated solution, is but slightly augmented by larger dilution, and hence in its influence upon the reaction studied may be put as a constant force tending to produce the change in question. Opposing this change, however, and therefore retarding the velocity of the decomposition, is the affinity of monochloracetic acid which, while much weaker than the hydrochloric at the beginning,

rapidly increases in strength in consequence of dilution, and consequently as the dilution increases holds the decomposition more and more completely in check.

The correctness of the above explanation has been called in question by Prof. Ostwald.[1] Unfortunately this criticism is not at hand. Through the kindness of Prof. Remsen, however, the following paragraph, which we quote below in full, and which according to the latter (Prof. Remsen) contains the essential elements of the criticism, has been brought to our notice:

"Der Verfasser diskutiert seine Versuche und gelangt zu einer etwas verwickelten Vorstellung, die hier nicht wiedergegeben werden soll. Dem Referent scheint eine andere Deutung wahrscheinlich. Die Frage, welcher von den beiden Anteilen des Salzes, der dissocierte oder der nicht dissocierte, der Zerzetzung erfährt, ist wahrscheinlich dahin zu beantworten, dass es der nicht dissocierte ist. Dieser nimmt aber mit steigender Verdünnung sehr schnell ab, und daraus würde sich die sehr starke Abnahme der Reaktionsgeschwindigkeit erklären."

After a very careful study of the above we are inclined to doubt if, after all, there is any essential difference between the explanation originally offered, it may be in rather complicated form, by one of us, and that so tersely expressed by Prof. Ostwald in the above paragraph.

From our standpoint it would seem to be an explanation of an explanation, if we may use this expression, rather than a totally different solution of the problem. If we understand him rightly, his view of the decomposition as applied to the case of potassium chloracetate would be somewhat as follows: When potassium chloracetate is brought into solution in water, dissociation takes place, and there exist in the solution at the same time and side by side ions of the dissociated portion of the salt (*viz.*, the potassium and the chloracet ion), together with a certain quantity of the undissociated portion of the salt composed of molecules of potassium chloracetate as such. Of these two portions it would seem that the latter only undergoes decomposition; it, however, rapidly decreases on dilution, and hence the marked falling off in the velocity of the reaction. If we accept this explanation, according to which the velocity of the reaction would be conditioned proportionately to the mass of undissociated potassium chloracetate

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[1] Ztschr. phys. Chem. **11**, 431.

present, then the question at once suggests itself, what will determine the quantity of undissociated salt at any given state of dilution? Now, plainly the amount of undissociated salt at any given dilution depends upon the quantity which is *dissociated*, and this latter will be directly proportional to the affinity of the chloracetic acid at that state of dilution, for the reason that the affinity of this and other acids depends upon the extent to which it and their salts are dissociable. It is just in this particular, therefore, that Prof. Ostwald's explanation, if carried to what would seem its rightful limit, presents many points of agreement with that put forward by one of us.

It would seem upon either hand ultimately to resolve itself into a question of relative affinities, and while it is to be admitted that Prof. Ostwald's conception of the decomposition, or at least the statement of it, has much in its favor so far as clearness is concerned, it is to be doubted if anything has really been gained, beyond a mere succinct expression, over the hypothesis as originally put forward. The true cause of the decomposition, whether it be of the whole or only a portion of the salt, is to be sought in the fact that the acid ion of hydrochloric acid, Cl, has under certain conditions sufficient strength to break down the molecule. The extent to which, however, this decomposition can take place depends very intimately upon the quantity of water present, for the reason that, according to Ostwald, the extent of the dilution determines the quantity of dissociated and non-decomposable salt, and therefore also the quantity of that which is undissociated and decomposable. But the extent of this dissociation is also a measure of the relative affinity of monochloracetic acid, and hence it is that the several velocities of the decomposition at different dilutions should be inversely proportional to the several coefficients of the affinity of this acid at corresponding dilutions.

In both explanations the dissociation of salts in aqueous solution is the central idea : the one stops at this point, the other goes on and attempts to establish connection between the decomposition under consideration and certain fundamental properties of a certain class of chemical compounds—properties which have already been proven to be dependent upon the amount of dissociation, *i. e.*, the affinity of acids.

If it were not known that the weaker acids increase in strength upon dilution, and, further, if this increase in strength were not

known to be due to the further dissociation produced in the compound by water, then indeed Prof. Ostwald's explanation might be said to be absolutely essential to a thorough understanding of this reaction.   As it is, however, the cause producing the change in the affinity of any given acid at various dilutions has been accepted as a well established principle, and the endeavor has been made to connect with the effects of this cause such changes in the velocity of the decomposition as have been observed.

It should be said in this connection that the hypothesis as originally put forward had for its object solely to account for the retarding influence of water upon the velocity of the decomposition.   It was not claimed for it that it would in any way account for the absolute amount of decomposition in any case, or offer any explanation for any constant difference which might be found to exist between the rates of decomposition of the salts of different acids—such, for example, as the marked and almost constant difference in the velocity of decomposition already shown to exist between the salts of monobrom- and monochloracetic acids.   On the other hand it is doubtful if any hypothesis, in the light of our present knowledge, can be advanced which will rightly embrace these two markedly different aspects of the phenomena here presented.   The three acids, hydrochloric, hydrobromic, and hydriodic, have practically the same affinity and yet they differ very widely in the order of stability.   Now so far as we are aware no theory seems capable of grasping at once these two sets of facts. About all that can be done at present is to hold up these two properties, activity and stability, as two entirely distinct and different properties of compounds.   Monochloracetic acid and monobromacetic acid furnish us with a parallel case; the salts of the latter decompose about twenty times as rapidly as do those of the former, and yet the coefficients of velocity of each exhibit very nearly the same relation among themselves at corresponding states of dilution.

The hypothesis under discussion was therefore, as stated above, originally advanced solely to explain the relation found to exist between the several coefficients of the velocity of the decomposition of the salts of any given acid at various states of dilution. This it has been found to do within certain limits.   As may be seen on p. 486, it has been found that, for the salts of monobrom- and monochloracetic acids, at normal, $\frac{1}{3}$-normal, and $\frac{1}{10}$-normal

states of dilution, the coefficients of the velocity of decomposition for each vary inversely as the coefficients of affinity of each of these acids at the several dilutions above named. It can scarcely be that the remarkable coincidence with which we are here dealing is simply a matter of chance or the result of accident. It may be argued against this hypothesis that the retarding effect produced by water stops far short of the point at which it, the water, exerts its greatest influence, by virtue of its dissociating power, upon the strength of monochlor- aud monobromacetic acids. For example, Ostwald has determined the affinity of these acids by means of their electrical conductivity, at the following dilutions, with these results:

	4 litres.	32 litres.	256 litres.
Monochloracetic acid	6.98	17.3	37.8
Monobromacetic acid	...	16.1	36.8

From this we see that, at a dilution of 256 litres, each of these acids is between five and six times as strong as it is at a dilution of 4 litres, and doubtless fully seven times as strong as it is at a dilution of 3 litres. Hence in the light of our hypothesis we ought to expect the coefficient of velocity for the decomposition of potassium chloracetate at the higher dilutions at which it has been studied, to sink as low as .0002 or .00025, which is about one-seventh of .0015—the coefficient of velocity for $\frac{1}{3}$-normal. As a matter of fact, however, no coefficient as small as either of the above has been obtained. As above stated, the minimum of decomposition seems to be reached at some dilution not very far removed from that of $\frac{1}{10}$-normal, at which the coefficient of velocity has been found to be .0008. From this dilution on the velocity of decomposition remains nearly constant.

It is to be remembered in this connection, however, that the coefficients of affinity of these acids for these higher states of dilution have been determined by the electro-chemical method, which in point of delicacy and nicety of measurement and in freedom from the disturbing influences of secondary reactions far exceeds that of any other chemical process; and it is much to be doubted if any strictly chemical process, such as the one now under investigation, will ever be found to yield such results, especially at these higher dilutions, as the constants obtained by purely physical methods would seem to require. This certainly has been found to apply to the determination of the affinity of acids. When

determined by strictly chemical methods, the affinities of strong acids as a rule appear too strong, and weak acids too weak, in consequence of the presence of neutral salts and the influence of secondary reactions.

As we have already seen, the reaction under consideration is by no means free from the disturbing influence of the products of the decomposition ; and while the results thus far obtained would seem to indicate that this disturbance is the same for different dilutions and therefore to be ignored, such may not indeed upon further investigation prove to be the case. On the other hand, it is easily conceivable that disturbing influences, each so small as to be imperceptible by the methods employed, might, by their combined action, altogether vitiate the final result.

In conclusion, it may be said that the present investigation was not undertaken with the view to establish or uphold any particular hypothesis, but simply to arrive, if possible, at the general law, if such there be, underlying such decompositions as have formed the subject of the present study.

The experimental difficulties in the way of arriving at results altogether satisfactory, while by no means insurmountable, are nevertheless such as to render progress along this line exceedingly slow. It has been found necessary, therefore, to modify the conditions and methods of experiment from time to time during the progress of the investigation. In the same way, as the investigation proceeds, it may also prove necessary to modify, or perhaps completely to change, the hypothesis originally advanced by way of explanation of the results first obtained. In the event that such indeed prove to be the case, we shall be found quite as willing to change our theoretical notions as we have been to modify for the better our methods of experimentation. Neither is to be regarded in any sense as final, but each rather as a means to an end.

A. AND M. COLLEGE OF KENTUCKY, LEXINGTON, *May*, 1893.

ON THE DOUBLE CHLORIDES OF LEAD AND AMMONIUM.

By Wyatt W. Randall.

In a paper published in 1889,[1] in which he calls attention to a law apparently holding good for all the so-called double halides of the alkali metals, Remsen says[2]: " . . . The examples given in the above tables are fair representatives of the whole class of double halides, except that all ammonium salts are omitted. The double halides formed with halogen salts of ammonium are very numerous, and many of them are quite complicated. There are, indeed, ammonium salts known, belonging to all the classes above mentioned, but there are many others which do not belong to these classes. Considering the power of ammonium salts in general to form complex compounds with metallic salts, one cannot avoid the conclusion that there is some power in nitrogen which makes the formation of these compounds possible. The position of the double halides containing ammonium is certainly exceptional."

His attention was, therefore, for the time being withdrawn, so far as actual investigation was concerned, from those compounds which contain the haloid salts of ammonium. In his second paper on this subject[3] he again declines strictly to consider these salts either as exceptions to or as confirmations of the law of composition, preferring to postpone the question of their nature and constitution until a more convenient season. At the suggestion of Professor Remsen I have made a beginning in the work of reinvestigating the composition of the double halides containing ammonium, by examining the case of the salts formed by the union of lead and ammonium chlorides. An additional interest is given to the investigation of these compounds by reason of the fact that, after most careful work, there was in no case obtained by Herty[4] or by Wells[5] a double halide of lead and potassium (or sodium) which did not accord with the law of composition stated by Remsen.

The only double chlorides containing lead and ammonium which I have been able to find described in the literature of the

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[1] This Journal **11**, 291.   [2] *Ibid.* **11**, 296.   [3] *Ibid.* **14**, 81.
[4] *Ibid.* **14**, 126.   [5] Am. J. Sci. **45**, 121.

subject are enumerated in a series of papers[1] by G. André, by whom they were prepared. The formulæ of these salts are, according to this author, (A) $PbCl_2.9NH_4Cl.1\frac{1}{2}H_2O$ ("$2PbCl,9Az$ $H_4Cl,3HO$"); (B) $2PbCl_2.11NH_4Cl.3\frac{1}{2}H_2O$ ("$4PbCl,11AzH_4Cl,$ $7HO$"); (C) $2PbCl_2.9NH_4Cl.2\frac{1}{2}H_2O$ ("$4PbCl,9AzH_4Cl,5HO$"); (D) $PbCl_2.6NH_4Cl.H_2O$ ("$PbCl,3AzH_4Cl,HO$"); (E) $PbCl_2.$ $18NH_4Cl.4H_2O$ ("$PbCl,9AzH_4Cl,4HO$"); (F) $PbCl_2.10NH_4Cl.$ H_2O ("$PbCl,5AzH_4Cl,HO$").

There is no one of these which is not an exception to Remsen's law of composition. One is naturally struck by the fact that no salt of comparatively simple formula is to be found in the list; nevertheless, double halides of complex character are by no means unknown, and the substitution of ammonium for sodium, potassium, etc., introduces a new factor likely to do away with the value of *a priori* reasoning.

Efforts have therefore been made to prepare the various double chlorides of lead and ammonium described by André, and, it may as well be said here, without success. The only definite double salts obtained will be shown to have been in accordance, as regards composition, with Remsen's law. I have called the salts described by André by the letters *A*, *B*, *C*, etc.

M. André seems to have relied entirely upon the results of his analyses to establish the definiteness of the salts which he prepared. There does not appear to have been any microscopic examination made; in fact hardly any reference to crystalline form, even, is to be noticed in his papers. Each of the salts described in this paper was subjected to crystallographic examination by Mr. E. B. Mathews, of the Geological Department of this University.[2] The results of these examinations will be given in their proper places.

Salt A.

Lead chloride dissolves more readily in a solution of ammonium chloride than in pure water, and with greater ease the more concentrated the solution. If now a solution of sal ammoniac which has been saturated in the cold be heated to boiling and saturated with lead chloride, there separates, on cooling, a salt which,

according to André, has the composition represented by the formula $PbCl_2.9NH_4Cl.1\frac{1}{2}H_2O$. To test the accuracy of this formula, efforts were made to prepare the salt by crystallization from solutions containing different amounts of lead chloride. A solution of sal ammoniac was made, saturated in the cold. Successive portions of this, of 250 cc. each, were taken and, after being raised to the boiling-temperature, were treated with definite quantities of crystallized chloride of lead. To the first portion were added 2 grams of lead chloride ; to the second, 3 ; to the third, 4 ; to the fourth, 5 ; to the fifth, 10 ; to the sixth, 15 grams. A clear solution was obtained practically at once in the first four cases ; in the fifth, the deposit disappeared after a few moments; in the last case, continued heating for a half-hour failed to produce a clear solution. An additional 50 cc. of the sal-ammoniac solution was therefore added and the heating continued. Ultimately the solution became perfectly clear. It would thus appear that the limit of solubility is reached when 15 grams of lead chloride are dissolved in 300 cc. (or 12.5 grams in 250 cc., to bring in accord with the other ratios). Each of these solutions was then set aside to cool, the beakers in which they were contained being placed within other beakers and surrounded with cotton-waste in order that the cooling might take place slowly and evenly. A deposit of crystals was formed in each case ; these deposits I have numbered from **1** to **6**, beginning with that deposited from the solution which contained but 2 grams of lead chloride, and ending with that which was saturated.

The salts **1–5** were deposited in fine, highly refracting, white crystals, and looked very much alike ; it will be shown that they possessed the same composition. Salt **6** crystallized out in much larger, more or less clear, orthorhombic pyramids. Under the microscope it was seen that **5** differed from **6** in having a larger development of the brachypinacoid and in having a basal plane. The $\frac{1}{m} P\underset{\infty}{\smile}$ faces, too, occur in different positions in the two salts.

Determinations of lead were made as follows : A weighed quantity of the salt was treated in a porcelain crucible with a few drops of pure concentrated sulphuric acid. Effervescence of hydrochloric acid having ceased, the crucible was placed on a triangle within an iron crucible and the temperature gradually raised until the ammonium sulphate had been volatilized. It was then carefully heated over the free flame for a few moments, allowed to

cool, again treated with acid and again heated in the iron crucible. The crucible and its contents were allowed to cool in a desiccator and were then weighed. In several instances another heating with acid and a second weighing were resorted to, but in no case was there a noteworthy difference in the two weights. In two instances the heating over the free flame was allowed to proceed until the crucibles were red-hot. There resulted a considerable dissociation of the lead sulphate and absorption of the lead by the glaze of the crucible. Further heating with sulphuric acid failed to remove the stain in the glaze, and so the results of these determinations were discarded.

The determinations of ammonia were made by decomposing a weighed quantity of the salt with an alkali and absorbing the ammonia evolved in a standard solution of hydrochloric acid. In the case of the first determination of ammonia in salt **6**, the salt was merely boiled with a strong solution of sodium hydroxide; in the case of the second, steam was conducted through the boiling alkali solution; afterwards milk of lime was used instead of caustic soda, and a current of steam steadily passed through the boiling liquid. These variations in the method employed may serve in part to explain the lack of perfectly satisfactory agreement among these three determinations. All the other determinations of ammonia were made with milk of lime as reagent.

The figures which follow are those obtained on analysis of salts **1-6**.

Salt 1.

I. 0.29156 gram salt gave 0.28852 gram $PbSO_4$.
II. 0.5205 gram salt gave 0.5144 gram $PbSO_4$.

Salt 2.

I. 0.31619 gram salt gave 0.31201 gram $PbSO_4$.
II. 0.41117 gram salt gave 0.40607 gram $PbSO_4$.

Salt 3.

I. 0.5555 gram salt gave 0.54671 gram $PbSO_4$.
II. 0.52587 gram salt gave 0.51888 gram $PbSO_4$.

Salt 4.

I. 0.37918 gram salt gave 0.37411 gram $PbSO_4$.
II. 0.52197 gram salt gave 0.51435 gram $PbSO_4$.

Salt 5.

I. 0.91077 gram salt gave 0.89967 gram $PbSO_4$.
II. 0.60435 gram salt gave 0.59779 gram $PbSO_4$.
III. 0.80643 gram salt gave 0.79875 gram $PbSO_4$.
IV. 0.80187 gram salt gave 0.02483 gram NH_3.
V. 0.5969 gram salt gave 0.01875 gram NH_3.

Salt 6.

I. 0.43165 gram salt gave 0.34003 gram $PbSO_4$.
II. 0.55922 gram salt gave 0.43943 gram $PbSO_4$.
III. 0.41978 gram salt gave 0.3326 gram $PbSO_4$.
IV. 0.67897 gram salt gave 0.05907 gram NH_3.
V. 0.41747 gram salt gave 0.03733 gram NH_3.
VI. 0.6905 gram salt gave 0.05957 gram NH_3.

Percentages.

	Salt 1.	2.	3.	4.	5.	6.
Pb.—I.	67.58	67.38	67.21	67.38	67.45	53.79
II.	67.49	67.44	67.38	67.29	67.55	53.66
III.	...	...	...	...	67.64	54.10
NH_3.—I.	...	...	...	...	3.09	8.70
II.	...	...	...	...	3.14	8.94
III.	...	...	...	...	...	8.63

Calculated for

	$PbCl_2.9NH_4Cl.1\tfrac{1}{2}H_2O$.	$(PbCl_2)_2.NH_4Cl$.	$PbCl_2.2NH_4Cl$.
Pb	26.32	67.91	53.76
NH_3	19.45	2.79	8.85

The chief conclusions to be drawn from these results are : (1) that the salts **1, 2, 3, 4** and **5** are identical and consist almost entirely of the compound $(PbCl_2)_2.NH_4Cl$, but having mixed in with this compound a trace of ammonium chloride which tends to lower the percentage of lead and to raise that of ammonia; (2) that salt **6** consists practically entirely of the compound $PbCl_2$. $2NH_4Cl$. Under the microscope the salts appear homogeneous. On heating salts **5** and **6** in dry test-tubes, there was scarcely a trace of water given off in the case of the latter and none whatever in the case of the former, although sublimation was very marked.

The conclusion seems, therefore, certain that no salt at all corresponding to that described by André and distinguished by the title *A*, was produced, and, as the conditions were varied to a

great degree in order that the proportion between the quantities of the two chlorides should give an opportunity for the production of a variety of salts, it seems evident that the salt *A* as prepared by André was a mixture and not a chemical unit.

Salts B, C, and D.

By saturating with lead chloride a solution of ammonium chloride which had been saturated at the boiling-point, and then allowing it to cool, André claims to have prepared three different double salts by varying slightly the conditions of the experiment. These salts I have designated by the letters *B*, *C*, and *D*, and their formulæ are, respectively, $2PbCl_2.11NH_4Cl\ 3\frac{1}{2}H_2O$; $2PbCl_2.9NH_4Cl.2\frac{1}{2}H_2O$; and $PbCl_2.6NH_4Cl.H_2O$. To be a little more accurate, salts *B* and *C* were obtained under identical conditions; while salt *D* consisted of those crystals which were first deposited, care being taken to remove them at once from the solution. The directions given for the preparation of these salts involve the solution of "about" 90 grams of lead chloride in a solution of "about" 200 grams of sal ammoniac in "about" 200 cc. of water. Water, even at the boiling-point, will not dissolve its weight of ammonium chloride, much less will this amount of the two chlorides be taken up at the same time. The directions cannot therefore be followed exactly. The method employed was the following :

100 cc. water was saturated at the boiling-point with ammonium chloride ; lead chloride was then added until the solution would no longer dissolve it. A very little hot saturated sal-ammoniac solution was then added to dissolve the slight residue of lead chloride, after which the liquid was heated until perfectly clear. The beaker was so arranged that the cooling took place very gradually. As soon as the deposition of crystals had fairly begun an attempt was made to decant the mother-liquor, the result being the mass almost solidified, and new layers of crystals settled upon those first deposited. This upper mass was carefully removed and the salt first deposited was separated as far as possible, was dried and examined. Under the microscope it was seen to be a mixture of an isotropic with an orthorhombic salt. The isotropic salt corresponded in its crystalline form with ammonium chloride, while a determination of the axial ratio of the orthorhombic salt showed it to be lead chloride. The former salt

was present in excess. An analysis of this salt ("7") gave the following figures:

    I. 0.2844 gram salt gave 0.14353 gram $PbSO_4$.
    II. 0.35156 gram salt gave 0.18295 gram $PbSO_4$.
    III. 0.30707 gram salt gave 0.15558 gram $PbSO_4$.

The percentages of lead are therefore 34.46, 35.54, and 34.6, respectively. André's salt, $2PbCl_2.11NH_4Cl.3\frac{1}{2}H_2O$, should contain 34.28 per cent. of lead. It therefore seems extremely probable that the salt obtained by André under these conditions was also a mixture, and not a definite compound.

In order to test this view more thoroughly, two more attempts were made to prepare a definite salt. Instead of decanting the solution, however, a circular piece of filter-paper cut so as to fit the beaker closely, was slipped into the solution as soon as the crystallization had proceeded far enough, and was allowed to sink down and rest upon the crystalline deposit. A perforated porcelain filtering-plate, previously warmed, was then lowered upon the paper to keep it in place and the crystallization allowed to proceed. After the liquid was cold the crystals which had been caught under the paper were separated and dried. They were marked "8" and "9," respectively. Both were found to be mixtures on examination under the microscope, and on analysis gave the following figures:

    I. 0.31627 gram of salt 8 gave 0.18545 gram $PbSO_4$.
    II. 0.50981 gram of salt 8 gave 0.29922 gram $PbSO_4$.
    I. 0.31288 gram of salt 9 gave 0.2068 gram $PbSO_4$.

The percentages of lead obtained were therefore: for salt 8, 40.04 and 40.08, and for salt 9, 45.13.

The only conclusion to be drawn from these results is, that if one were to perform the experiment a sufficient number of times, salts of almost any desired composition could be obtained. Analysis alone is incapable of determining with certainty the question of such a salt's individuality.

All the efforts made to prepare from lead chloride definite double chlorides of lead and ammonium of the kind described by André, by following his directions—or such modifications of these as seemed necessary or advisable—were therefore unsuccessful. There are, however, other salts described by him as formed in a solution of ammonium chloride which has been treated with litharge and heated. These salts will be here designated as *E*

and F, their composition being thus represented by André: E, $PbCl_2.18NH_4Cl.4H_2O$; and F, $PbCl_2.10NH_4Cl.H_2O$. In addition to these, the salt D, $PbCl_2.6NH_4Cl.H_2O$, is described as a product of this action under certain conditions. To put it more definitely: if a solution of 100 grams of ammonium chloride in 200 cc. of water is heated to boiling, treated with 25 grams of litharge, boiled a few moments to dissolve the oxide, filtered, and allowed to cool, the salt E is said to be deposited. If the boiling is continued $1\frac{1}{2}$ hours, F is the product; if the solution is boiled 3 hours, D is deposited. It will be seen that the salt with the largest proportion of ammonium chloride is that formed when the amount of lead chloride in the solution is very slight, and that as the decomposition of the litharge proceeds, salts with a larger proportion of lead chloride are produced. Judging by the results obtained when lead chloride itself was added to solutions of ammonium chloride saturated in the cold—in other words, comparatively dilute solutions—this should be the case if the deposit were a *mixture;* but *not*, if the salt formed were a definite compound. For the salt $(PbCl_2)_2.NH_4Cl$ was obtained in each experiment of the first series until the solution was saturated with lead chloride, when the salt $PbCl_2.2NH_4Cl$ was formed. The value of such an argument is, of course, not great; nevertheless, if it is found to agree with the results of experiments, it must be taken into account.

The litharge used was prepared by precipitating a solution of lead nitrate with ammonium carbonate, and then heating the well-washed lead carbonate to 300° in an air-bath. The proportions given above were used, and a series of salts was obtained which were designated by the numbers **10–14**. After the litharge had been added to the hot sal-ammoniac solution, the boiling was continued but a few minutes, in the case of salts **10** and **11**. The solution was then quickly filtered with the aid of a hot-water funnel, was again heated until the lead chloride which had begun to crystallize out had redissolved, and was then allowed to cool slowly, as in the former series of experiments, care being taken, as before, to secure the crystals first deposited. In the preparation of salts **12**, **13** and **14**, the only variation on this method was, that the boiling with the litharge was continued for $1\frac{1}{4}$, $1\frac{3}{4}$, and 3 hours, respectively.

On examination under the microscope it was seen that each of

these salts was a mixture. **10** and **11** were composed very largely of the regular crystals of ammonium chloride. The lead chloride present had crystallized first, and was almost entirely in the form of enclosure in the crystals of sal ammoniac. The following figures were obtained on analysis:

0.23242 gram salt **10** gave 0.15188 gram $PbSO_4$.

0.25134 gram salt **11** gave 0.1775 gram $PbSO_4$.

The percentages of lead are : for **10**, 44.62 ; for **11**, 48.22.

Under these conditions the salt obtained by André had a composition to be represented by the formula $PbCl_2.18NH_4Cl.4H_2O$, having only 15.76 per cent. of lead. It appears, therefore, very likely that had the growth of the ammonium-chloride crystals about the lead chloride been allowed to proceed without hindrance, similar mixtures could have been obtained in these cases. In the case of salt **12** it was seen that the two constituents were present as before, the orthorhombic being in the form of an enclosure within the regular. There was apparent also a slight difference in habit in the regular constituent. The proportion of the two when examined under the microscope was seen to be about half-and-half. No analysis of this salt was made. Salts **13** and **14** were found to be very much alike. Each appeared almost homogeneous when examined under the microscope; the regular constituent being present only in very small amount. In the finer portion of **13** the ammonium-chloride crystals seemed by actual count to make up only 2–5 per cent. of the whole. Analyses of **13** gave the following figures :

I. 0.41035 gram salt gave 0.30119 gram $PbSO_4$.

II. 0.29413 gram salt gave 0.21534 gram $PbSO_4$.

III. 0.28432 gram salt gave 0.20632 gram $PbSO_4$.

IV. 0.34766 gram salt gave 0.25145 gram $PbSO_4$.

V. 0.31104 gram salt gave 0.03267 gram NH_3.

VI. 0.24866 gram salt gave 0.03528 gram NH_3.

Percentages.

	I.	II.	III.	IV.	V.	VI.
Pb	50.12	50.00	49.55	49.39	...	...
NH_3	...	...	...	...	10.50	14.19

The fact that these analyses were made in the order given may, to some extent at least, account for the uniform decrease in the percentage of lead and rise in that of ammonia ; the finer, heavier

particles of the lead salt tending, as the vessel was handled, to sink to the bottom of the weighing-glass and leave the larger, lighter ammonium chloride at the surface, whence it was poured off into the crucible, etc. The percentages agree with those required for a mixture of one part of ammonium chloride with about two parts of the salt $PbCl_2.2NH_4Cl$.

In the case of salt **14** the crystallization seemed to have progressed more slowly and evenly ; the salts were quite distinct and the individual crystals were well formed. Mr. Mathews therefore undertook a mechanical separation of the two constituents under the microscope, making use of the finer portions of the mixture. The regular crystals were weeded out and were labeled "**15**," while the practically homogeneous, orthorhombic portion ("**16**") was analyzed with the following results :

I. 0.24692 gram salt gave 0.24032 gram $PbSO_4$.

II. 0.37836 gram salt gave 0.36934 gram $PbSO_4$.

	Calculated for $(PbCl_2)_2.NH_4Cl$.	Found. I.	II.
Pb	67.91	66.46	66.66

It appears, therefore, that salt **16** is practically identical with salts **1–5**, or, in other words, that the same product is obtained whether we dissolve lead chloride or lead oxide in a hot, unsaturated solution of ammonium chloride ; provided that in the latter case the boiling be continued for sufficient time to decompose most of the oxide. The amount of ammonium chloride deposited with the double salt depends upon the concentration, method of crystallizing, etc.

SUMMARY.

As a result of this work it seems justifiable to say that the salts described by André as definite compounds were, on the contrary, mixtures of various compositions. The only salts which on microscopic examination proved to be homogeneous, definite substances were shown to be in harmony, as regards composition, with Remsen's law ; their formulæ being respectively $(PbCl_2)_2.NH_4Cl$ and $PbCl_2.2NH_4Cl$. These results acquire fresh interest in view of the fact that they seem to indicate that some, at least, of the double salts containing ammonium follow the same law of composition as those of the other alkalies.

It is hoped in the near future to examine the double bromides of lead and ammonium. These, like the chlorides, have been

described by André as possessing formulæ utterly at variance with Remsen's Law of Composition.

In conclusion, I should express my indebtedness to Professor Remsen for many useful suggestions given by him during the course of the work.

JOHNS HOPKINS UNIVERSITY, *May*, 1893.

DERIVATIVES OF NITROGEN HALOGEN COMPOUNDS.

SECOND PAPER.

BY FELIX LENGFELD AND JULIUS STIEGLITZ.

In a preliminary paper[1] we stated that two compounds are formed by the action of sodium methylate on succinimide bromide. Their composition seemed to indicate that the lower-melting is formed by the replacement of bromine by methoxyl and the addition of one molecule of methyl alcohol, and the other by an analogous replacement of bromine by a succinimide residue,

$$\left(-N<\begin{array}{c}COCH_2\\ |\\ COCH_2\end{array}\right),$$

and a similar addition of methyl alcohol. Further investigation has shown that such is the case and that *a molecular rearrangement occurs in the course of the reaction.* The method of formation suggested the constitution $\begin{array}{c}CH_2.CO_2CH_3\\ |\\ CH_2.CON<\begin{array}{c}H\\ OCH_3\end{array}\end{array}$ for the compound melting at $33.5°$. It was therefore treated both with acids and with alkalies to obtain a-methylhydroxylamine. It yielded β-amidopropionic acid, however, instead. This alone does not prove that it is not an hydroxylamine derivative. Lossen[2] and his pupils found that some hydroxamic acids readily lose carbon dioxide and give amido-compounds—dibenzhydroxamic acid, for

[1] This Journal **15**, 215.   [2] Ann. Chem. (Liebig) **175**, 313 *et seq.*

instance, giving aniline. Lassar-Cohn[1] obtained anthranilic acid by the action of alkali on phthalylhydroxylamine. Beckmann[2] has shown that similar rearrangements are effected by acids. Toward mild alkalies the substance acts like the methyl ether of a mono-basic acid, but this does not prove that it is not

$$CH_2.NH.CO_2CH_3$$
$$|$$
$$CH_2.CO_2.CH_3,$$
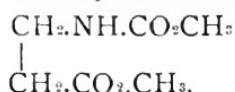
the carbalkoxyl group (—COOR) of the carbamic ethers being very stable.

The methyl ether of carbomethoxy-β-amidopropionic acid was therefore prepared from methyl-β-amidopropionate and methyl-chlorformate,

$$2NH_2.CH_2.CH_2.CO_2.CH_3 + ClCO_2.CH_3 =$$

$$CH_3.CO_2.CH_2.CH_2.NH.CO_2.CH_3 + HCl.NH_2.CH_2.CH_2.CO_2.CH_3.$$
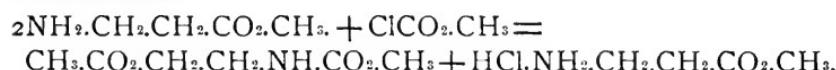
The two compounds were identical. There is, therefore, when sodium methylate acts on succinimide bromide, a rearrangement similar to that produced by the action of caustic alkalies on amide bromides, as first shown by Hofmann,[3] and more fully studied by Hoogewerf and Van Dorp.[4] The latter chemists have likewise prepared β-amidopropionic acid from succinimide by means of bromine and an alkali.[5] The formation of methyl carbomethoxy-β-amidopropionate may be represented as follows:

$$
\begin{array}{l}
N = C \\
\;|\quad\;| \\
Br\;\;CH_2 \\
\;\;\;\;\;| \\
\;\;\;\;CH_2 \\
\;\;\;\;\;| \\
O = C
\end{array}
\Big\rangle O \rightarrow
\begin{array}{l}
N = C.Br \\
\;\;\;\;| \\
\;\;\;CH_2 \\
\;\;\;\;\;| \quad O \\
\;\;\;CH_2 \\
\;\;\;\;\;| \\
\;\;\;O = C
\end{array}
+
\begin{array}{l}
Na.OCH_3 \\
\\
H \\
| \\
O.CH_3
\end{array}
= NaBr +
$$

$$
\begin{array}{l}
N = C{<}^{OCH_3}_{OH} \\
\;|\\
CH_2 \\
\;|\\
CH_2 \\
\;|\\
CO_2.CH_3
\end{array}
= NaBr +
\begin{array}{l}
NH.CO.OCH_3 \\
\;\;\;| \\
\;\;CH_2 \\
\;\;\;| \\
\;\;CH_2 \\
\;\;\;| \\
\;\;CO_2.CH_3.
\end{array}
$$
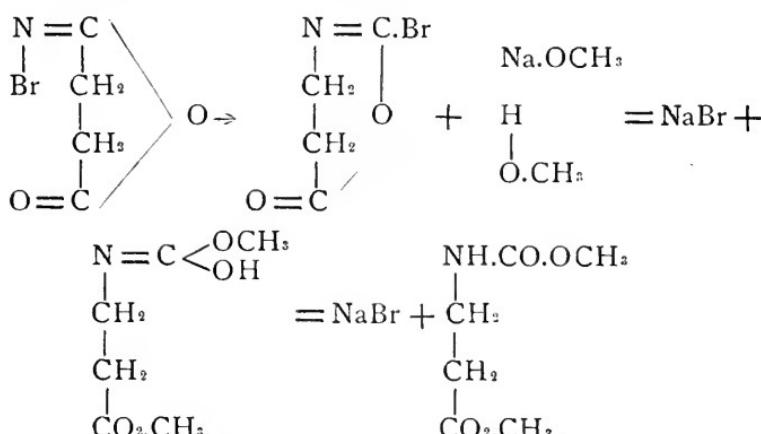
This scheme agrees best with the rearrangement of nitrogen compounds studied by Beckmann and others.

[1] Ann. Chem. (Liebig) **205**, 303.
[2] Ber. d. chem. Ges. **19**, 988; **20**, 1507; Ann. Chem. (Liebig) **274**, 1, etc.
[3] Ber. d. chem. Ges. **15**, 762.   [4] Recueil trav. chim. **9**, 33; **10**, 4.   [5] *Ibid.* **10**, 5.

It is, however, possible that the reactions are the following:

$$CH_2CO \Big\rangle NBr + HOCH_3 = \begin{matrix} HN.C\!\!\nearrow^{\!\!O}\!\!\searrow_{Br} \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO_2.CH_3 \end{matrix}$$

$$\begin{matrix} HN\!-\!C\!\!\nearrow^{\!\!O}\!\!\searrow_{Br} \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO_2.CH_3 \end{matrix} + NaOCH_3{}^1 = NaBr + \begin{matrix} HN.CO_2.CH_3 \\ | \\ H_2C \\ | \\ H_2C \\ | \\ CO_2.CH_3. \end{matrix}$$
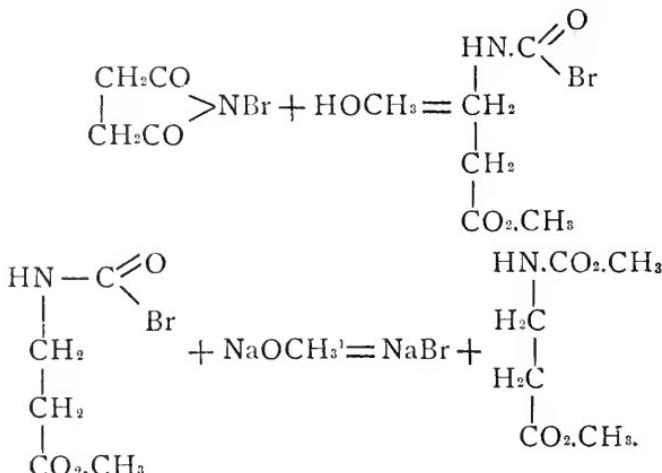
The study of methyl carbomethoxy-β-amidopropionate made it seem probable that the compound melting at 65.5° is the dimethyl ether of succinylo-β-ureidopropionic acid,

$$HO_2C.CH_2.CH_2.CONH.CONH.CH_2.CH_2.CO_2H,$$

a similar molecular rearrangement having taken place.[2] On saponification with alkalies it yields succinic and β-ureidopropionic acids. Treated with hydrochloric acid it gives a compound $C_4H_6N_2O_2$, melting at 272°.[3] The composition of this substance agreeing with that of β-lactylurea which should be readily formed from dimethyl succinylo-β-ureidopropionate, β-lactylurea was made synthetically and the two were found to be identical. There can therefore be no doubt that the substance melting at 65.5° is $CH_3.O_2C.CH_2.CH_2.CONH.CONH.CH_2.CH_2.CO_2.CH_3$. This establishes the view already expressed,[4] that sodium succinimide can play the same rôle as sodium methylate.

The reaction is probably as follows:

$$\begin{matrix} N \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO \end{matrix} \!\!=\!C.Br \;\; NaN\!\!\nearrow^{\!\!COCH_2}\!\!\searrow_{COCH_2} + \begin{matrix} H \\ | \\ OCH_3 \end{matrix} + HO.CH_3 =$$

---
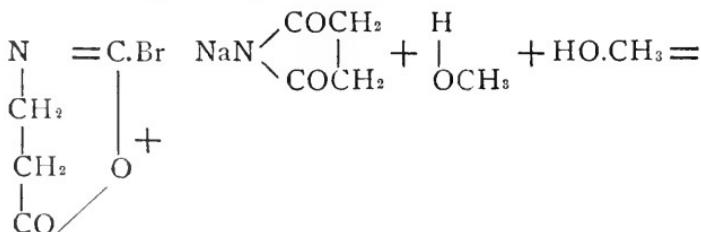
[1] The rearrangement is effected by the sodium methylate.

[2] Its formation is similar to that of acetylmethylurea observed by Hofmann in the action of sodic hydrate on acetamide bromide. Ber. d. chem. Ges. **14**, 2725.

[3] This Journal **15**, 221.   [4] *Ibid.*

$$N = \overset{\overset{\displaystyle OH}{\diagup}}{\underset{\displaystyle \overset{|}{CH_2}}{C}} .N.CO.CH_2.CH_2.CO_2.CH_3 + NaBr, \quad \text{or}$$

$$\underset{\displaystyle \overset{|}{CH_2.CO_2.CH_3}}{\overset{|}{}}$$

$$HN\overset{\overset{\displaystyle O}{\diagup\!\!\!\diagup}}{\underset{\displaystyle \overset{|}{CH_2}}{C}} \diagdown NH.CO.CH_2.CH_2.CO_2.CH_3 + NaBr.$$
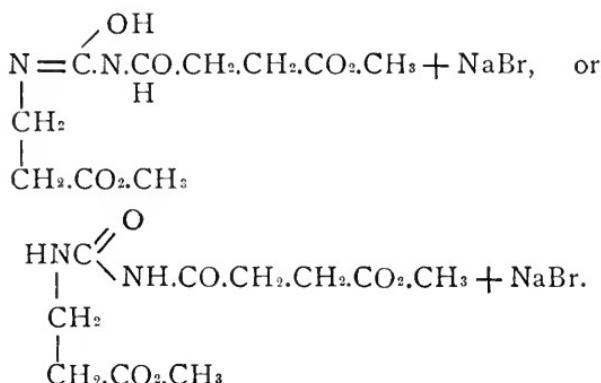
$$\underset{\displaystyle \overset{|}{CH_2.CO_2.CH_3}}{\overset{|}{}}$$

Experimental Part.

Methyl carbomethoxy-β-amidopropionate, $CH_3O_2C.NH.CH_2.$ $CH_2CO_2CH_3.$—This compound has already been described by us.[1] In portions of 3 grams it was heated to 120°–130° in sealed tubes with hydrochloric acid (7–8 grams) for four hours. On opening the tubes a gas, identified as carbon dioxide, escaped in quantity. The liquid contents of the tubes were evaporated on the water-bath to a syrup which, on cooling, solidified to a crystal-line mass. This was washed with chloroform, placed over sodic hydrate to remove traces of hydrochloric acid, recrystallized from boiling absolute alcohol, washed first with alcohol and then with ether, and finally brought on clay plates. Addition of ether to the alcoholic filtrate precipitated more of the same substance. An-alysis and its behavior showed it to be the *hydrochloride of β-amidopropionic acid,* $HCl.NH_2.CH_2.CH_2.CO_2H.$ It forms white crystals which under a microscope are seen to be irregular plates. It melts at 122.5°. Analysis gave the following figures :

0.2557 gram substance gave 0.1541 gram H_2O and 0.2671 gram $CO_2.$

	Calculated for $C_3H_8NO_2Cl$.	Found.
C	28.69	28.49
H	6.37	6.69

Decomposition of methyl carbomethoxy-β-amidopropionate by hydrochloric acid at ordinary pressures, or by potassic hydrate and subsequent addition of hydrochloric acid, gave the same salt together with some carbomethoxy-β-amidopropionic acid, which, being easily soluble in chloroform, can be separated from it

[1] This Journal **15,** 217.

without difficulty. The reaction is therefore not complete. In sealed tubes the yield, however, is quantitative according to the equation,

$$\begin{array}{l} \mathrm{NH.CO_2.CH_3} \\ | \qquad\qquad\qquad + 2\mathrm{H_2O} + \mathrm{HCl} = \\ \mathrm{CH_2.CH_2.CO_2.CH_3} \end{array}$$

$$\begin{array}{l} \mathrm{NH_2.HCl} \\ | \qquad\qquad\qquad + \mathrm{CO_2} + 2\mathrm{CH_3OH}. \\ \mathrm{CH_2.CH_2.COOH} \end{array}$$
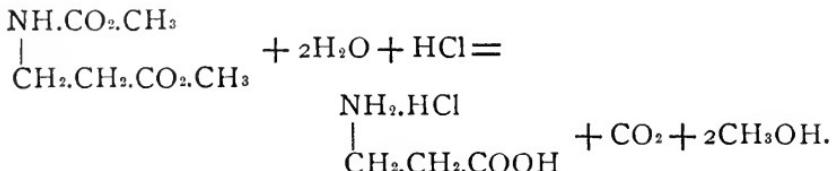
The substance thus obtained is undoubtedly the hydrochloride of β-amidopropionic acid. We obtained the acid from it and made it from the acid prepared by Hoogewerf and Van Dorp's[1] method. It crystallizes easily and can be used as an aid in identifying β-amidopropionic acid.

β-Amidopropionic acid.—4 grams of the hydrochloride were dissolved in water, boiled with an excess of lead oxide,[2] evaporated to dryness on the water-bath, the powdered mass extracted with boiling water, which was cooled, filtered, and the lead precipitated by hydrogen sulphide. The residue on evaporation was dried on a clay plate. It weighed 2.5 grams and was pure β-amidopropionic acid. It melts with decomposition and evolution of gas at 206°–207°, heating rapidly. The melting-point remains constant after repeated recrystallization. Analysis gave:

I. 0.2173 gram substance dried at 105° gave 0.1603 gram H_2O and 0.3204 gram CO_2.

II. 0.1767 gram substance dried at 105° gave 24.5 cc. moist nitrogen at 16° and 746.7 mm.

	Calculated for $C_3H_7NO_2$.	I.	II.
C	40.44	40.26	...
H	7.87	8.19	...
N	15.73	...	15.93

As Hoogewerf and Van Dorp give for β-amidopropionic acid the melting-point 196°, being 16° higher than that found by Mulder,[3] we prepared some of the acid by their method. It was identical with that described above, melting with decomposition at 206°. To prepare large quantities of the acid it was found convenient to modify Hoogewerf and Van Dorp's method. 20 grams succinimide is added to a solution of 32 grams bromine in 900 grams of

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[1] Recueil trav. chim. **10**, 5.　　[2] Heintz: Ann. Chem. (Liebig) **156**, 36.
[3] Ber. d. chem. Ges. **9**, 1903.

a 10-per cent. solution of potassic hydrate, the liquid slowly heated to 60° and kept at that temperature for two hours. To the cooled solution hydrochloric acid is added in excess, and the whole evaporated to dryness on the water-bath. The residue is exhausted with absolute alcohol (best in Soxhlet's apparatus), dry hydrochloric acid passed in, allowed to stand over night, decanted from sodic chloride, and evaporated to a syrup. This consists mainly of ethyl succinate and the hydrochloride of ethyl β-amidopropionate, and usually crystallizes on standing. It is dissolved in boiling water, a hot solution of baric hydrate added, boiled for half an hour and filtered. The barium is carefully precipitated with sulphuric acid, and the solution, after concentration, treated with lead oxide as above. The acid thus obtained is washed with hot absolute alcohol to remove any succinic acid that remains. The yield is about 65 per cent. of the theoretical.

It became necessary in the course of our work to prepare a number of simple derivatives of β-amidopropionic acid not hitherto described.

Sulphate of β-amidopropionic acid.—On evaporating a solution containing equivalent quantities of β-amidopropionic and sulphuric acids, fine colorless crystals of this salt remain. It may be purified by washing first with very little water and then with absolute alcohol. It melts with some decomposition at 150°, is easily soluble in water, difficultly in alcohol, and under the microscope is seen to crystallize in short, thick prisms. It does not lose in weight at 100°. Analysis gave: 0.4117 gram substance gave 0.345 gram $BaSO_4$.

	Calculated for $(C_3H_7NO_2)_2H_2SO_4$.	Found.
H_2SO_4	35.50	35.25

Hydrochloride of methyl β-amidopropionate, $HCl.NH_2.CH_2.$
$CH_2.COOCH_3$.—β-Amidopropionic acid was allowed to stand twenty-four hours in a saturated solution of hydrochloric acid in methyl alcohol; the solution was then evaporated and the residue purified by fractional precipitation from chloroform by ligroïn and from methyl alcohol by ether. The salt forms white shining scales, which are hygroscopic and melt at 94°–95°.

0.1785 gram substance gave 16.5 cc. moist nitrogen at 24.5° and 731 mm.

	Calculated for $C_4H_9O_2N.HCl$.	Found.
N	10.03	10.00

Hydrochloride of ethyl β-amidopropionate, $HCl.NH_2.CH_2.CH_2.$ $COOC_2H_5$, was first prepared and analyzed by Hoogewerff and Van Dorp, who, however, do not give its melting-point. We obtained it first on recrystallizing from boiling alcohol impure hydrochloride and amidopropionic acid formed by the decomposition of methyl carbomethoxyamidopropionate by hydrochloric acid. The hydrochloric acid had not been entirely removed and consequently etherification took place. Owing to the lack of data for identifying it, analyses were made.

I. 0.1632 gram substance gave 13.0 cc. moist nitrogen at 12° and 728 mm.

II. 0.0956 gram substance gave 0.0897 gram AgCl.

III. 0.2554 gram substance gave 0.188 gram H_2O, (CO_2 lost).

	Calculated for $C_5H_{11}O_2N.HCl$.	Found.
H	7.82	8.18
N	9.12	9.12
Cl	23.13	23.20

It was also prepared in the same way as the methyl ether. It crystallizes in white plates melting at 65.5°, and is easily soluble in water, alcohol and chloroform.

Synthesis of methyl carbomethoxy-β-amidopropionate.—β-Amidopropionic acid, probably on account of its salt-like nature, does not react at ordinary temperatures with methyl chlorformate. Its amine-like ethers and alkali salts react with great ease.

5.58 grams (2 mol.) of the hydrochloride $CH_3OOC.CH_2.CH_2.$ $NH_2.HCl$ dissolved in 75 cc. chloroform was shaken for ten to fifteen minutes with 4.65 grams (1 mol.) of dried silver oxide. To the filtrate 1.95 grams (1 mol.) of methyl chlorformate dissolved in 50 cc. absolute ether was added. Some hydrochloride of methyl β-amidopropionate was precipitated almost immediately. More ether was added and the hydrochloride filtered off. On evaporating the filtrate, an oil remained which distilled without decomposition at 140° under 15 mm. pressure, became solid on cooling and then melted at 33.5°. All its properties are those of methyl carbomethoxy-β-amidopropionate obtained from succinimide bromide. Like it, it gives when shaken with lime-water an acid melting at 77°; with ammonia, the amide described below, melting at 142°. The reaction is

$2CH_3OOC.CH_2.CH_2.NH_2. + Cl.CO.OCH_3 =$
$CH_3OOC.CH_2.CH_2.NH_2.HCl + CH_3OOC.CH_2.CH_2.NH.COOCH_3.$
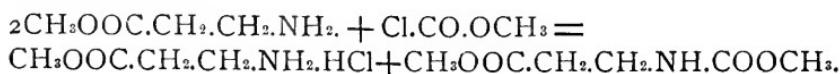
The ether was also obtained from its synthetically-prepared acid.

Carbomethoxy - β - amidopropionic   acid, $\begin{array}{l} CH_2.NH.COOCH_3 \\ | \\ CH_2.COOH, \end{array}$
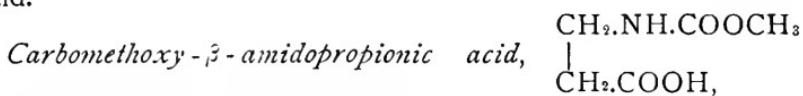
obtained from its ether by saponification, has already been described by us.[1] Its melting-point is 77°–77.5°. It may be obtained directly from potassium amidopropionate and methyl chlorformate:

$$2KOOC.CH_2.CH_2.NH_2 + Cl.CO.OCH_3 =$$
$$\begin{array}{l} CH_2.NH.COOCH_3 \\ | \qquad\qquad\qquad + KCl + NH_2.CH_2.CH_2.COOH. \\ CH_2.COOK \end{array}$$
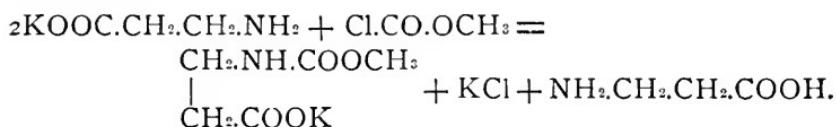
1.9 grams amidopropionic acid were dissolved in a solution of 1.2 grams potassic hydrate in 3.5 cc. water and 1 gram methyl chlorformate added. The reaction was instantaneous, the mixture becoming quite warm. After diluting and washing with chloroform, an excess of hydrochloric acid was added and the mixture exhausted with chloroform. The product, after recrystallization, melts at 77° and is identical with the acid previously described. It is quite a stable compound, being one of the products of the action of potassic hydrate and concentrated hydrochloric acid on the ether. It is monobasic and yields corresponding salts.

Barium carbomethoxy-β-amidopropionate, $(CH_3.OOC.NH.CH_2.$ $CH_2.COO)_2Ba.$—1.5 grams of the acid were dissolved in a little water and 1.5 grams (an excess) of barium carbonate added. When no more carbon dioxide was given off the solution was filtered, placed in a vacuum for a day, again filtered from a trace of baric carbonate, and left to evaporate over sulphuric acid. A sticky mass remained which soon became solid. It was powdered, washed with chloroform and dried over phosphoric anhydride. It is very soluble in water and melts with decomposition at 90°.

0.4224 gram substance gave 0.192 gram $BaCO_3$.

	Calculated for $(C_5H_8NO_4)_2Ba$.	Found.
Ba	31.93	31.61

The silver salt, $CH_3OOC.NH.CH_2.CH_2.COOAg$, prepared from the barium salt, is a curdy white precipitate which becomes dark on exposure to light and is sparingly soluble in water. For

[1] This Journal **15,** 219.

analysis it was dried on a clay plate and then in a desiccator in a dark place.

0.1709 gram substance gave 0.073 gram Ag.

	Calculated for $C_5H_8NO_4Ag$.	Found.
Ag	42.54	42.71

Ethyl carbomethoxy-β-amidopropionate, $CH_3.OOC.NH.CH_2.$ $CH_2.COOC_2H_5.$—9 grams of acid were dissolved in 45 grams of alcohol. Hydrochloric acid was then passed in, and, after standing, the alcohol evaporated. The residue was purified by dissolving in chloroform and precipitating with ligroïn. Most of the dark oil precipitated distilled at 135°–137°, under 14 mm. pressure, as a colorless oil which solidified in a freezing-mixture and melted at 15.5°. Shaken with milk of lime it yields carbomethoxyamidopropionic acid. Analyses:

I. 0.2663 gram substance gave 0.1775 gram H_2O and 0.4634 gram CO_2.

II. 0.1767 gram gave 12.5 cc. moist nitrogen at 755.5 mm. and 16.5°.

	Calculated for $C_7H_{13}NO_4$.	Found.
H	7.43	7.82
C	48.00	47.46
N	8.00	8.21

Carbomethoxy-β-amidopropionamide, $CH_3OOC.NH.CH_2.CH_2.$ $CONH_2.$—2 grams of methyl carbomethoxyamidopropionate were warmed with about 12 cc. concentrated aqueous ammonia to 55°–60° for 15 minutes, and the solution then allowed to evaporate in a vacuum-desiccator. Colorless crystals remained, which were dried on a clay plate, washed with ether, and dissolved in a boiling mixture of equal volumes of absolute alcohol and chloroform. On adding a second volume of chloroform and sufficient ligroïn, the amide was precipitated in microscopic needles. From water or ammonia it crystallizes in broad orthorhombic plates with sharply defined lines of cleavage. Large crystals of the amide are deposited when the ether is dissolved in five times its weight of concentrated ammonia solution and allowed to stand a few days. The amide melts at 142.5°. Analyses:

I. 0.200 gram substance, dried at 100°, gave 0.1284 gram H_2O and 0.3014 gram CO_2.

II. 0.1242 gram substance gave 21 cc. moist nitrogen at 20.5° and 739.7 mm.

	Calculated for $C_5H_{10}N_2O_3$.	Found.
C	41.10	41.10
H	6.85	7.13
N	19.18	19.06

The well-known stability of the urethanes and the extreme instability of the carbamic acids indicated almost beyond a doubt that the carboxyl of the acid $C_5H_9O_4N$ is not attached to nitrogen and that therefore its constitution is that given, *viz.*

$$\begin{array}{l} CH_2.NH.COOCH_3 \\ | \\ CH_2.COOH \end{array} .$$
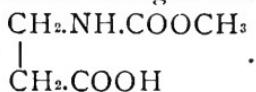
This is shown directly by the behavior of the mixed ethers.

Methyl carbethoxy-β-amidopropionate, $\quad \begin{array}{l} CH_2NH.COOC_2H_5 \\ | \\ CH_2.COOCH_3 \end{array} .—$
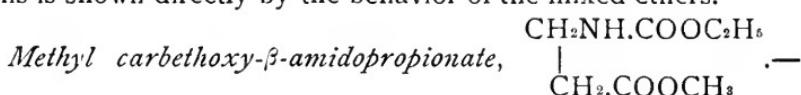
12.9 grams of the hydrochloride of methyl amidopropionate were treated[1] with 10.7 grams silver oxide and 5 grams ethyl chlorformate :

$$2CH_3OOC.CH_2.CH_2.NH_2 + Cl.CO.OC_2H_5 =$$

$$CH_3OOC.CH_2.CH_2.NH_2.HCl + \begin{array}{l} CH_2.NH.COOC_2H_5 \\ | \\ CH_2.COOCH_3 \end{array} .$$
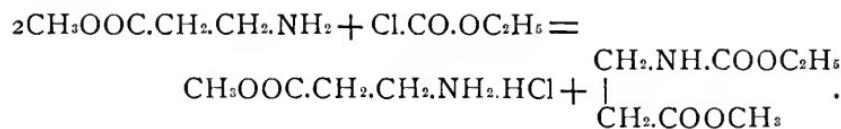
The oily product distilled at 134°–137° under 15 mm. pressure, and then solidified in a freezing-mixture. It melts below 0°. 0.204 gram substance gave 14.5 cc. moist nitrogen at 18.5° and 733 mm.

	Calculated for $C_7H_{13}NO_4$.	Found.
N	8.0	7.89

On being saponified with lime-water, the methyl group is split off and

Carbethoxy-β-amidopropionic acid, $C_2H_5OOC.NH.CH_2.CH_2.COOH$, is formed. It was obtained as an oil, which solidified in the cold, and was purified by dissolving in chloroform and precipitating with ligroïn. It forms colorless crystals melting at 59°.

0.2221 gram substance gave 17.4 cc. moist nitrogen at 20.5° and 733.5 mm.

	Calculated for $C_6H_{11}NO_4$.	Found.
N	8.70	8.66

Carbethoxy-β-amidopropionamide, $C_2H_5OOC.NH.CH_2.CH_2.CO.NH_2$.—1 gram of the ether was mixed with 7 grams concentrated aqueous ammonia, heated to 60° and evaporated over sulphuric

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[1] See page 510.

acid. Recrystallized by precipitating with ligroïn from a mixture of alcohol and chloroform, it forms colorless crystals which melt at 120.5°.

0.1607 gram substance gave 23.9 cc. moist nitrogen at 10° and 745 mm.

	Calculated for $C_6H_{12}N_2O_3$.	Found.
N	17.50	17.49

These results afford absolute proof that in the ether

$$\begin{array}{l} CH_2.NH.COOCH_3 \quad (I) \\ | \\ CH_2.COOCH_3 \qquad (II) \end{array},$$
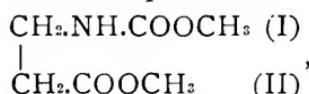
it is the group $COOCH_3$ (II) that is reactive.

Dimethyl succinylo-β-ureidopropionate,

$$\begin{array}{cc} CH_2.NH.CO.NH.CH_2 \\ | \qquad\qquad\qquad | \\ CH_2.COOCH_3 \quad CH_2.COOCH_3, \end{array}$$
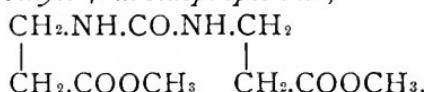
is formed when sodium methylate acts on succinimide bromide in concentrated methyl-alcoholic solution. It has already been described by us.[1] It melts at 65.5°. By mild saponification it yields succinic acid and β-ureidopropionic acid. 3 grams of the ether were shaken with milk of lime at intervals for three hours, the solution filtered, nearly all the calcium precipitated with oxalic acid, and the filtrate evaporated at 50° under diminished pressure. The residue, which was washed with alcohol and dried on a clay plate, proved to be β-ureidopropionic acid.[2] The alcoholic washings left on evaporation succinic acid.

As it is extremely improbable that so mild an alkali causes a molecular rearrangement, the above decomposition must be:

$$\begin{array}{l} CH_2.NH.CO.NH.CO.CH_2 \\ | \qquad\qquad\qquad | \qquad\qquad + 3H_2O = \\ CH_2.COOCH_3 \qquad CH_2.COOCH_3 \end{array}$$

$$\begin{array}{ll} CH_2.NH.CO.NH_2 & HOOC.CH_2 \\ | \qquad\qquad\qquad + \qquad | \qquad + 2CH_3OH, \\ CH_2.COOH & HOOC.CH_2 \end{array}$$
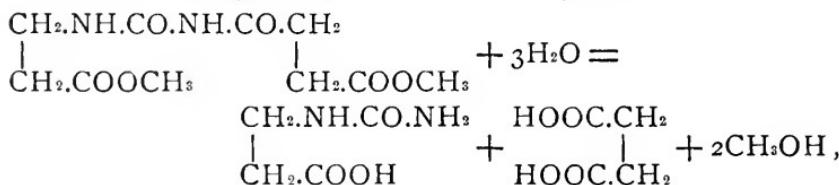
and the constitution of the compound must be that given.

Decomposed with concentrated hydrochloric acid, dimethyl succinylo-β-ureidopropionate yields succinic acid and β-lactylurea, hydrochloric acid readily condensing β-ureidopropionic acid (see below):

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[1] This Journal **15**, 220.　　　[2] See page 515.

$$CH_2.NH.CO.NH.CO.CH_2$$
$$| \qquad\qquad | \qquad\qquad + 2H_2O =$$
$$CH_2.COOCH_3 \qquad CH_2.COOCH_3$$

$$CH_2.NH.CO \qquad CH_2.COOH$$
$$| \qquad\qquad | \quad + \quad | \qquad + 2CH_3OH .$$
$$CH_2.CO.NH \qquad CH_2.COOH$$
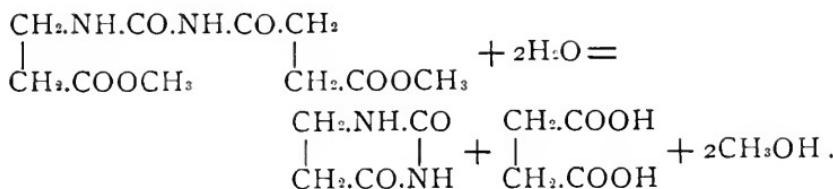
The reaction has been described by us.[1] The β-ureidopropionic acid and β-lactylurea thus obtained are identical with preparations which we have made synthetically.

Methyl β-ureidopropionate, $NH_2.CO.NH.CH_2.CH_2.COOCH_3$.
—To a cold solution of 2.5 grams (1 mol.) of the hydrochloride of methyl amidopropionate 1.5 grams (1 mol.) of potassium cyanate are added, and the mixture slowly evaporated on a water-bath. The powdered residue is washed with ether and then exhausted with hot chloroform. The chloroform gives on evaporation a syrup, which soon crystallizes. From benzene it was precipitated by ligroïn as a colorless oil which crystallizes on standing in silky needles, which under a microscope are seen to be long, flat prisms. It melts at 66.5°, is easily soluble in water, alcohol and chloroform, difficultly in ether, ligroïn, and benzene even when warm.

0.1279 gram substance gave 22.7 cc. moist nitrogen at 23.5° and 733.2 mm.

	Calculated for $C_5H_{10}N_2O_3$.	Found.
N	19.18	19.27

It is isomeric with carbomethoxy-β-amidopropionamide, described above.

β-Ureidopropionic acid, $NH_2.CO.NH.CH_2.CH_2.COOH$. — 3 grams of methyl β-ureidopropionate were allowed to stand for 6 hours with 5 grams (an excess) of baric hydrate in 100 cc. of water. The barium, with the exception of a trace, was precipitated with sulphuric acid, and the filtrate evaporated at 40°–50° under diminished pressure. Three crops of crystals were obtained, of which the first contained some β-lactylurea, the third a little barium salt. The intermediate product was pure acid; it was brought on a clay plate and dried in a desiccator.

0.1045 gram substance gave 19.5 cc. moist nitrogen at 21° and 741.8 mm.

	Calculated for $C_4H_8N_2O_3$.	Found.
N	21.21	20.97

It is not easily soluble in cold water, difficultly in organic solvents, and dissolves readily in hot water, the alkalies, and alkali carbonates. It melts with evolution of gas at 170°–171°. It is very unstable, readily losing water and forming β-lactylurea. This takes place even when its aqueous solution is evaporated on a water-bath with some hydrochloric acid. On heating 10 to 15 minutes, first at 160° and then at 170°, condensation takes place almost quantitatively.

$$\begin{array}{c} CH_2.NH.CO.NH_2 \\ | \\ CH_2.COOH \end{array} = \begin{array}{c} CH_2.NH.CO \\ | \qquad | \\ CH_2.CO.NH \end{array} + H_2O.$$
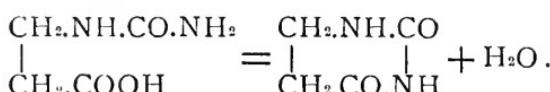
Unlike the sulphates of other amido-acids,[1] β-amidopropionic acid sulphate does not react smoothly with potassium cyanate. On mixing solutions of the two, effervescence and the odor of cyanic acid were observed, and no ureidopropionic acid or lactylurea was found in the product obtained. This behavior seems to be due to the smaller influence of the amido-group in the β- than in the α-position on the acid radicle, so that the weaker cyanic acid cannot combine with the base. For this reason the methyl ether of the acid was used instead, as above. It was afterwards found that β-amidopropionic acid itself reacts with the greatest ease with

potassium cyanate, forming the salt $\begin{array}{c} CH_2.NH_2.(HNCO) \\ | \\ CH_2.COOK \end{array}$. This,
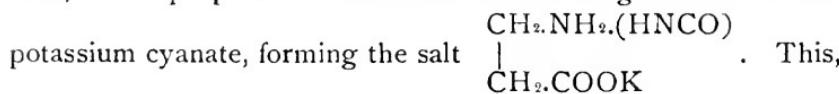
when its solution is treated with acids, gives off cyanic acid. On evaporating its aqueous solution it is converted into

Potassium β-ureidopropionate, $NH_2.CO.NH.CH_2.CH_2.COOK.$ —Solutions of 2 grams (1 mol.) of β-amidopropionic acid and 1.85 grams (1 mol.) potassium cyanate were mixed and slowly evaporated on a water-bath. From the syrupy residue, on standing, large colorless crystals separated. They were removed from the mother-liquor, brought on a clay plate and immediately placed in a desiccator. The salt is extremely hygroscopic, softens at 80° and melts at 100°. Heated at 100°–105° for one hour, it lost less than 1 per cent. in weight.

0.146 gram substance, dried at 105°, gave 0.0743 gram K_2SO_4.

	Calculated for $C_4H_7KN_2O_3$.	Found.
K	22.93	22.85

[1] Menschutkin: Ann. Chem. (Liebig) **153**, 83; etc.

Evaporated on the water-bath with dilute hydrochloric acid, it is converted quantitatively into β-lactylurea. This method of obtaining β-ureidopropionic acid and β-lactylurea from the amido-acid and potassium cyanate gave a very good yield and suggests that it may be extensively used with advantage for this purpose. β-ureidopropionic acid is also one of the products of the action of mild alkalies on dimethyl succinyloureidopropionate.

β-Lactylurea,
$$\begin{array}{c} \text{CH}_2.\text{NH.CO} \\ | \qquad\qquad | \\ \text{CH}_2.\text{CO.NH} \end{array}$$
, as obtained from the ureido-acid,

was purified by recrystallizing from hot 50-per cent. alcohol. Dried at 100°, it fused at 272° with decomposition, and proved identical in all respects with the product obtained from dimethyl succinyloureidopropionate and already described.[1]

0.1128 gram synthetically-prepared substance gave 23.8 cc. moist nitrogen at 12° and 745.2 mm.

	Calculated for $C_4H_6N_2O_2$.	Found.
N	24.56	24.64

It has a neutral reaction and is insoluble in sodic carbonate, but dissolves readily in caustic alkali, like other ureïdes. Its silver salt,

Silver β-lactylurea,
$$\begin{array}{c} \text{CH}_2.\text{NH.CO} \\ | \qquad\qquad | \\ \text{CH}_2.\text{CO.N.Ag} \end{array}$$
, was prepared by dissolving

0.8 gram (a slight excess) substance in 3.6 cc. of a 10-per cent. solution of potassic hydrate, filtering from a slight undissolved residue, and adding a concentrated solution of 1.2 grams silver nitrate. The heavy white curdy precipitate was washed with a little cold water, brought on a clay plate and dried over sulphuric acid in a dark place. It becomes slightly darker on exposure to light, and is somewhat soluble in cold water.

0.3186 gram substance gave 0.1545 gram Ag.

	Calculated for		Found.
	$C_4H_5AgN_2O_2$.	$C_4H_7AgN_2O_3$.[2]	
Ag	48.87	45.19	48.49

As the molecular rearrangement of the nitrogen derivatives

$$\begin{array}{c} -\text{C} = \text{N} \\ | \qquad | \\ Y \qquad X \end{array}$$
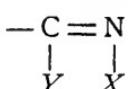
[1] This Journal **15**, 221. [2] $NH_2.CO.NH.CH_2.CH_2.COOAg$.

is supposed to depend on the relative negative and positive character of the groups X and Y, we propose to vary group Y, so as to obtain, if possible, substances in which the rearrangement does not occur, and to use other nitrogen halogen compounds for the same purpose.

ON THE DECOMPOSITION OF DIAZOBENZENE SULPHATE IN ISOAMYL ALCOHOL.

By W. R. ORNDORFF AND C. G. HOPKINS.

It has been shown by Remsen and Orndorff[1] that when diazobenzene sulphate is decomposed by heating it in absolute ethyl alcohol, two reactions take place simultaneously, yielding phenylethyl ether in the first case, and benzene in the second. The normal reaction appears to be the one forming phenylethyl ether according to the equation

$$C_6H_5.N_2.HSO_4 + HOC_2H_5 = C_6H_5.OC_2H_5 + H_2SO_4 + N_2.$$
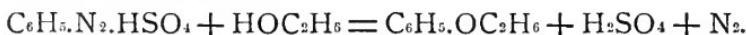
The second reaction, yielding benzene, takes place according to the equation

$$C_6H_5.N_2.HSO_4 + C_2H_6O = C_6H_6 + N_2 + H_2SO_4 + C_2H_4O,$$

and appears to be subsidiary to the first, as the yield of phenylethyl ether is much greater than that of benzene.

Quite recently Parks[2] has shown that when paradiazoorthotoluenesulphonic acid is decomposed with methyl alcohol, paramethoxyorthotoluenesulphonic acid is the only product of the reaction. The second reaction, which we should expect to yield orthotoluenesulphonic acid, does not take place here. When paradiazoorthotoluenesulphonic acid is decomposed in ethyl alcohol, Remsen and Palmer[3] have shown that the two reactions take place simultaneously, yielding both ethoxytoluenesulphonic acid and toluenesulphonic acid, although the amount of the latter was small in comparison with the amount of the former. Thinking that the difference in the conduct of this diazo

[1] This Journal **9**, 387.   [2] *Ibid.* **15**, 320.   [3] *Ibid.* **8**, 243.

compound when decomposed in methyl and ethyl alcohols might be due to differences in the two alcohols, the following experiments on the decomposition of diazobenzene sulphate in isoamyl alcohol were undertaken by the authors. It was thought that, since the diazo compounds when decomposed with methyl alcohol gave only the methoxy compound, while, when decomposed with ethyl alcohol, both reactions take place, yielding the ethoxy compound as well as the sulphonic acid ; that if higher alcohols of the methyl alcohol series were used, the second reaction—the so-called hydrogen reaction—would alone take place. Unfortunately this has not proven to be the case ; yet as a new reaction of the diazo compounds was discovered in the course of this work, these results are here recorded.

The diazobenzene sulphate was made by the method of Knoevenagel[1] and decomposed in absolute isoamyl alcohol (boiling at 130°–131°) in portions of 20 grams. The dry diazobenzene sulphate, together with about three times its weight of isoamyl alcohol, was placed in a round-bottomed flask which was connected with a return-condenser and heated on a water-bath. About 400 grams of the diazobenzene sulphate were thus decomposed. The decomposition took place rapidly and smoothly below the boiling-point of water, generally beginning at 70°. After the decomposition had apparently ceased the heat was increased until the water in the bath was boiling. Gas was given off freely during the decomposition, and in several cases this gas smelled strongly of benzene. Some of this gas was collected and carefully examined. It was found to be pure nitrogen containing a very small amount of isoamyl-alcohol and benzene vapors. The flask containing the diazo compound and the isoamyl alcohol was weighed before and after the decomposition, and the loss in weight due to the escaping gas was found in every case to agree very well with that required by the theory. During the decomposition of the diazo compound the isoamyl alcohol becomes dark red in color, probably owing to the formation of some azo dyestuff.

After the decomposition of the diazo compound was completed the separate portions were united and treated with caustic-soda solution to remove the sulphuric acid, preliminary experiments having shown that unless this was done the sulphuric acid would act on the isoamyl alcohol, forming secondary products, such as

[1] Ber. d. chem. Ges. **23**, 2994.

amylene and diamylene. The isoamyl alcohol solution of the decomposition-products of the diazobenzene sulphate was then subjected to fractional distillation through a Hempel tube. The distillate separated into two layers, an upper one consisting largely of isoamyl alcohol and a lower one which was nearly all water. On redistilling this aqueous layer through a Hempel distilling-tube a liquid was obtained boiling at 92°–93°, which had the odor of an aldehyde and whose solution in water reduced an ammoniacal solution of silver nitrate very readily. This liquid was identified as isovaleric aldehyde.

The upper layer of the first distillate was also redistilled through a Hempel distilling-tube. A product was obtained which boiled below 90° and which was shown to be benzene by its boiling-point, physical properties and ready formation of dinitrobenzene when treated with a mixture of nitric and sulphuric acids.

Only a few cubic centimeters of the benzene and the isovaleric aldehyde were obtained and it is quite evident that they are not the chief products of the reaction.

Besides the benzene and the isoamyl alcohol the upper layer gave two other products when refractioned several times, one boiling at 183°–184° (uncorr.) and which solidified when cooled with ice-water, and the other boiling at 215°–220° (uncorr.). The liquid boiling at 183°–184° was formed in large quantity and was the principal product of the decomposition. It melted at about 30°, after it had been once solidified and separated from the oil which accompanied it, and gave all the reactions for phenol. After being carefully purified by redistillation and recrystallization it was analyzed. The results follow:

I. 0.4664 gram substance gave 1.3110 grams CO_2 and 0.2930 gram H_2O.

II. 0.4247 gram substance gave 1.1910 grams CO_2 and 0.2780 gram H_2O.

	I.	II.	Theory for C_6H_6O.
C	76.66	76.48	76.60
H	6.98	7.27	6.38
O (by difference)	16.36	16.25	17.02

Vapor-density determinations by the Victor Meyer method gave the following results:

	I.	II.
Weight of substance	0.154 gram.	0.1125 gram.
Barometer	740 mm.	740 mm.
Volume of air expelled	39.8 cc.	29.7 cc.
Temperature of air when measured	21° C.	20.5°.

	I.	II.	Theory for C_6H_6O.
Vapor-density found (referred to air)	3.39	3.31	3.26

From these results and the properties of the substance it was concluded that the chief product of the reaction is undoubtedly phenol.

The product boiling at 215°–220° was also purified by redistillation and analyzed. The results follow:

I. 0.2188 gram substance gave 0.6404 gram CO_2 and 0.1889 gram H_2O.

II. 0.2548 gram substance gave 0.7436 gram CO_2 and 0.2204 gram H_2O.

	I.	II.	Theory for $C_6H_5.O.C_5H_{11}$.
C	79.82	79.59	80.50
H	9.59	9.61	9.80
O (by difference)	10.59	10.80	9.70

A vapor-density determination by the Victor Meyer method gave the following result:

Weight of substance	0.1335 gram.
Barometer	740 mm.
Volume of air expelled	20.7 cc.
Temperature of air when measured	21°

		Theory for $C_6H_5.O.C_5H_{11}$.
Vapor-density found (referred to air)	5.66	5.67

These results show that the substance is isoamylphenyl ether. The amount of this substance formed was very small.

The products of the decomposition of diazobenzene sulphate in isoamyl alcohol are, then, phenol, isoamylphenyl ether, benzene, isovaleric aldehyde, nitrogen and sulphuric acid. The isoamylphenyl ether is formed by the decomposition of the diazobenzene sulphate according to the equation

$$C_6H_5.N_2|HSO_4 + H|OC_5H_{11} = C_6H_5.O.C_5H_{11} + N_2 + H_2SO_4,$$
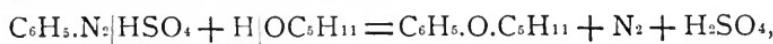
free nitrogen and sulphuric acid being formed at the same time.

The benzene and isovaleric aldehyde result from the decomposition of the diazo salt as follows :

$$C_6H_5.N_2.HSO_4 + C_5H_{12}O = C_6H_6 + C_5H_{10}O + H_2SO_4 + N_2.$$

Regarding the formation of phenol, the authors believe that the decomposition may be correctly represented by the following equation:

$$C_6H_5.N_2|HSO_4 + C_5H_{11}|OH = C_6H_5OH + C_5H_{11}.HSO_4 + N_2,$$
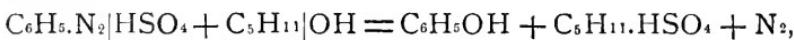
the products being phenol, isoamyl acid sulphate and free nitrogen. In support of this view of the formation of phenol it may be stated that the isoamyl alcohol used in the decompositions boiled constantly at $130°–131°$ and was shown to be absolutely anhydrous. The diazobenzene sulphate was dry and crystalline. It was washed with alcohol and then with ether before drying, so that it may be assumed that it was free from water. Isoamyl acid sulphate was found among the products of the reaction, but unfortunately it could not be determined whether it resulted from this reaction or from the action of the sulphuric acid, set free in the other reactions, on the isoamyl alcohol. There seems, however, to be no good reason why sulphuric acid should be formed here in preference to isoamyl acid sulphate, and as the formation of the latter explains in a satisfactory manner the production of phenol, it has been assumed here.

Experiments were then undertaken upon the decomposition of the diazo compound obtained from metanitraniline. The metanitrodiazobenzene sulphate was made by the method of Knoevenagel and decomposed in isoamyl alcohol, according to the directions given above. Nitrobenzene, isovaleric aldehyde and nitrogen were formed in the decomposition and were readily identified, but no metanitrophenol could be isolated from the products. A very large quantity of a brown dyestuff was formed which was shown to be metadinitrooxyazobenzene, $C_6H_4(NO_2).$ $N_2.C_6H_4(OH).NO_2$. This was probably formed by the metanitrophenol combining as soon as formed with metanitrodiazobenzene sulphate according to the equation :

$$C_6H_4{<}^{NO_2}_{N_2.HSO_4} + C_6H_4{<}^{NO_2}_{OH} =$$
$$C_6H_4{<}^{NO_2(m)}_{N_2C_6H_3}{<}^{NO_2}_{OH(m)} + H_2SO_4.$$
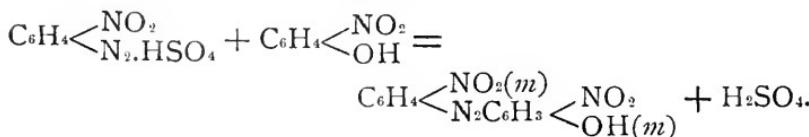
The metanitrophenol itself being formed according to the reaction represented by the equation

$$C_6H_4{<}{NO_2 \atop N_2.}|HSO_4 + C_5H_{11}|OH =$$
$$C_6H_4{<}{NO_2 \atop OH(m)} + C_5H_{11}HSO_4 + N_2.$$
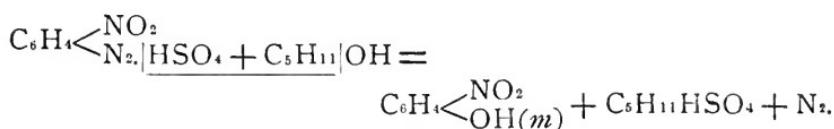
Further investigation of this interesting reaction is in progress.

ITHACA, *May*, 1893.

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A NEW CLASS OF ORGANIC ELECTROSYNTHESES.

BY S. P. MULLIKEN.

Although the number of organic compounds that have been subjected to electrolysis is large, the organic acids containing the carboxyl group together with their salts remain the only class in regard to whose electrolytic decomposition-products generalizations of much interest have been reached. The products obtained on passing the electric current through solutions of other organic . substances have for the most part owed their origin to secondary reactions,—generally oxidations or reductions. Such secondary reactions were invariably observed by the earlier experimenters in this field, when the futile attempt was made to confer the property of electrical conductivity on a non-electrolyte by adding to it a mineral acid or base. Thus it was early discovered that the electrolysis of alcohol containing sulphuric acid yields aldehyde, formed by the action on the alcohol of the electrolytic oxygen liberated, while nitrobenzene mixed with weak alkaline or saline solutions is so readily reduced by electrolytic hydrogen that the electrolysis of such a mixture is a process that has been patented.[1]

This article contains the first results obtained in a series of electrosynthetic experiments still in progress, which were begun by the author while a fellow of Clark University, more than two years ago. These experiments were undertaken with a view to deter-

[1] Ber. d. chem. Ges. **16**, 96.

mine whether certain organic compounds not belonging to the carboxylic acid or salt type, possessing acid properties, but not generally recognized as electrolytes, could be electrolyzed; and if so, whether the negative ions liberated from them could be caused to unite with one another by employing methods similar to those used by Crum-Brown and Walker in their interesting syntheses of dibasic acids from sodic ethylic malonate and its homologues.[1]

The group of substances possessing these acidic properties is a large and heterogeneous one. Among its members may be mentioned ketonic derivatives like acetylacetone and acetoacetic ether; sodium salts, like that of malonic ether; imides, and nitro-paraffin derivatives. These compounds are all exceedingly weak acids and their salts are unstable. Acetylacetone, which is one of the strongest acids of the group, expels carbon dioxide from carbonates. Acetoacetic and ethylacetoacetic ethers are, however, so weak that, according to the recent molecular-conductivity measurements of Walden, even acetic acid is by comparison an excellent conductor:[2]

$v.$	$\mu.$	$v.$	$\mu.$	$v.$	$\mu.$
128	16.99	128	1.18	128	0.068
256	23.82	256	1.20	256	0.070
Acetic acid.		Acetoacetic ether.		Ethylacetoacetic ether.	

$v =$ dilution in litres per gram-equivalent.
$\mu =$ molecular conductivity.

Diethylic malonate, $CH_2(CO_2C_2H_5)_2$, does not conduct electricity at all, and it was only by using its sodium salt, which is probably represented[3] by the symbol $C{<}^{OC_2H_5}_{ONa}$, that it became possible to $\overset{\|}{HC.CO_2C_2H_5}$ employ it in electrolytic experiments.

The products obtained in all the electrosyntheses thus far made are the same that one would expect to be formed by the action of iodine on the sodium or silver compounds of the substances electrolyzed. Thus:

$$2C_7H_{11}O_4Na + 2I = 2NaI + C_2H_2(CO_2C_2H_5)_4, \text{ and}$$
Sodium diethylic malonate.   Ethylic ethanetetracarboxylate.

$$2C_7H_{11}O_4Na \text{ (electrolyzed)} = 2Na + C_2H_2(CO_2C_2H_5)_4.$$
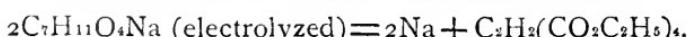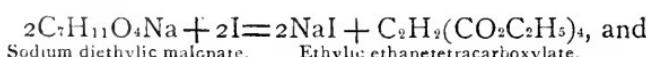
[1] Ann. Chem. (Liebig) **261**, 107.   [2] Walden: Ber. d. chem. Ges. **24**, 2025.
[3] Nef: Ann. Chem. (Liebig) **266**, 114.

The yields from the iodine reaction, when this could be used, were generally better than those given by the electrical method. In the synthesis of ethylic ethanehexacarboxylate, however, a fair yield of an interesting body was obtained by the electrical method, when the iodine reaction signally failed. The two methods are therefore to be regarded as supplementary to each other, and it is to be hoped that a careful study of the conditions favorable to electrosynthesis of this kind will result in improvements in the electrical method that will lead to larger yields.

The electrical apparatus for the early experiments was simple, but not altogether satisfactory. The electrolytic cells were thin-walled glass cylinders 3–5 cm. in diameter, having capacities of from 30–100 cc. The anodes were spirals of platinum wire 1–2 mm. in diameter, and the cathodes rectangular strips of platinum foil almost wide enough, when folded into cylinders, completely to surround the spiral anodes. Accidental contacts between the electrodes were provided against by inserting a narrow glass ring between them at the bottom of each cell. The wires connected with the electrodes passed through perforations in the corks closing the cylinders. The necessarily high electrical resistance offered by the solutions always caused some heating. Each cylinder was therefore surrounded by a cooler through which water circulated. When the quantity of a solution was small, or the resistance very high, the capacity of a cell was diminished and the electrodes brought nearer together by winding the platinum spiral about a stout glass cylinder closed at its lower end. With this arrangement, by establishing a circulation of cold water within the inner cylinder, an effective internal cooler could also be improvised. The use of a platinum spiral having a comparatively small surface as anode—only about one-tenth of the surface of the cathode—is a device of Crum-Brown and Walker's for increasing the density of the current at the anode in order to give the most favorable conditions for the union to molecules of the nascent radicles there liberated.

The current was furnished by a battery of 49 "crowfoot" gravity-elements set up in series. This form of battery was employed because a dynamo and storage cells were not available, and a constant current could be obtained from it for weeks together without requiring much attention to keep it in order. Its internal resistance was very high (often two ohms to the cell), so that the

current obtainable from it was always weak—a disadvantage which was partly remedied by multiplying the number of electrolytic cells and connecting them in parallel circuit.

Electrolysis of Sodic Diethylic Malonate (Ethylic Ethanehexa-

$$carboxylate).-2 \underset{HC.CO_2C_2H_5}{\overset{C<\overset{OC_2H_5}{ONa}}{||}} = Na_2 + 2 \underset{CO_2C_2H_5}{\overset{CO_2C_2H_5}{\underset{|}{CH}}} \rightarrow \underset{CH.(CO_2C_2H_5)_2}{\overset{CH.(CO_2C_2H_5)_2}{|}}.$$
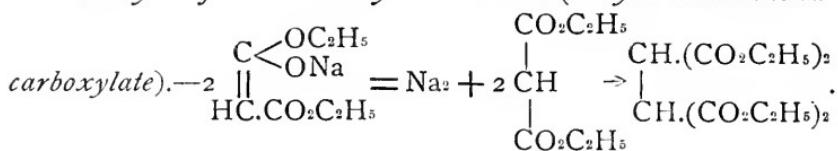
This electrolysis was performed in an alcoholic solution. To prevent the accumulation of uncombined sodium ethylate during the passage of the current, this solution was prepared so as to contain malonic ether as well as its sodium compound. The sodium set free at the cathode reacted on the free malonic ether present to form a fresh quantity of sodium salt, and the strength of the electrolyte was thus maintained constant for a long time.

3 grams of sodium were dissolved in 40 grams of well-cooled malonic ether and the solution made up to 100 cc. by adding absolute alcohol. A current of one-sixth of an ampère was then passed through the solution for 23 hours. Hydrogen was disengaged at the cathode, while little or no gas appeared at the other pole. The clear, yellowish solution was neutralized with acetic acid, evaporated on the water-bath, and the residue extracted with ether. An oil was thus obtained which fractionation under a pressure of 15 mm. showed to consist almost entirely of two constituents. One of these boiled between 90° and 100° and was malonic ether. The other boiled between 190° and 210° and solidified in a freezing-mixture. Its weight amounted to about 25 per cent. of that of the malonic ether present in solution as sodium salt at the beginning of the electrolysis. Crystallized from alcohol, this compound formed a compact mass of long, white needles, melting at 73°. According to an analysis it contained 52.69 per cent. of carbon and 6.53 per cent. of hydrogen. A comparison of its properties and appearance with those of a specimen of pure ethylic " acetylenetetracarboxylate " prepared by Bischoff's method[1] from iodine and the sodium salt of malonic ether, left no doubt that the two bodies were really identical. The body obtained by Conrad's method melted at 76° and should contain 52.83 per cent. of carbon and 6.92 per cent. of hydrogen. The slightly

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[1] Bischoff, Rach : Ber. d. chem. Ges. **17**, 2781.

lower melting-point observed for the body obtained by the electrical method seemed due to a mere trace of some impurity that could not easily be removed by crystallization.

Electrolysis of Sodic Ethylic Methanetricarboxylate (Ethylic Ethanehexacarboxylate).—Ethylic methanetricarboxylate, $CH.(CO_2C_2H_5)_3$, and its sodium salt were prepared by the method described by Michael.[1] The sodium salt was used because the pure ester is such a poor conductor that an electrolysis of its solution was found impracticable. The following reaction may be assumed to take place when the current traverses solutions of the sodium salt :

$$2 \underset{C(CO_2C_2H_5)_2}{\overset{C<^{OC_2H_5}_{ONa}}{||}} = Na_2 + 2\overset{|}{C}(CO_2C_2H_5)_3 \rightarrow \underset{C-(CO_2C_2H_5)_3}{\overset{C-(CO_2C_2H_5)_3}{|}} .$$

The sodium salt obtained by Michael's method is a white powder readily soluble in water and without decomposition—unlike the corresponding salt of malonic ether, which water immediately splits into sodic hydrate and malonic ether. The stability of such solutions is, however, only relative; for on standing for a few hours, even in closed vessels from which the air is excluded, all the ethylic methanetricarboxylate present separates out as an oily layer. Three portions of sodium salt weighing 15 grams each, were dissolved in 30 cc. of cold distilled water. Each portion was electrolyzed in a small cell provided with an efficient water-cooler. A current of one-third of an ampère was passed through the solutions for 24 hours, although a shorter electrolysis would doubtless have given equally good results, since after two or three hours all the ester that had at first been combined with sodium seemed to have separated out at the bottoms of the cells. Carbon dioxide was evolved at the anode, and a considerable quantity of acid sodic carbonate separated out with the oil. The alkaline solution above the oil possessed a very peculiar pungent odor.

The contents of the three cells were united, neutralized with dilute sulphuric acid and shaken out with ether. The oil dissolved by the ether was distilled under a pressure of 24 mm. Boiling began at 90° and was interrupted at 230°. The residue in the flask was an oily mass of the consistency of butter, which weighed 6 grams. The neck of the distilling-flask was dotted with small semi-spher-

[1] A. Michael: J. prakt. Chem. [2] **37**, 476.

ical aggregates of a crystalline solid, and a small quantity of this same substance separated from that portion of the distillate boiling between 190° and 230°, when this was cooled down to −10°. The lower-boiling fractions were mixtures of ethylic methanetricarboxylate and ethylic malonate. The ethylic malonate and acid sodic carbonate were probably formed by the following secondary reactions which took place in the cell during the electrolysis, and have necessarily no direct connection with the electrolytic process proper :

(*a*). $C_{10}H_{15}O_6Na + H_2O = C_{10}H_{16}O_6 + NaOH.$

(*b*). $C_{10}H_{16}O_6 + NaOH + H_2O =$
$$CH_2(CO_2C_2H_5)_2 + C_2H_5OH + NaHCO_3.$$
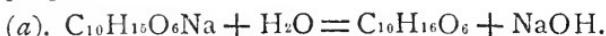
Reaction (*b*) has already been mentioned by Conrad and Guthzeit.[1] The solid compound present in the two highest-boiling fractions was purified by slow crystallization from ethereal solution. The hard, white crystalline crusts obtained were repeatedly washed with small quantities of dry ether. The compound melted at 101° (corrected). It is freely, but very slowly soluble in alcohol and in ether. Elementary analysis gave results agreeing with the numbers expressing the percentage-composition of the hexethylic ether of ethanehexacarboxylic acid.

I. 0.3186 gram substance gave 0.6062 gram CO_2 and 0.1844 gram H_2O.

II. 0.2468 gram substance gave 0.4676 gram CO_2 and 0.1432 gram H_2O.

	Calculated for $C_{20}H_{30}O_{12}$.	Found. I.	II.
C	51.95	51.90	51.80
H	6.49	6.43	6.45
O	41.56	41.67	41.75
	100.00	100.00	100.00

The molecular weight of the ether determined by the freezing-point method was found to be 442; the molecular weight calculated for the compound $C_{20}H_{30}O_{12}$ is 461.

The constitution of this ether has been definitely proved to correspond to the formula above given to it, by experiments just completed in this laboratory by Mr. J. B. Weems, an account of which will soon appear in this Journal. With the exception of the butanehexacarboxylic ether of Bischoff and Rach[2] it is the first

[1] Ann. Chem. (Liebig) **214**, 34 and 37.   [2] Ber. d. chem. Ges. **17**, 2786.

derivative of a hexacarbonic acid that has been prepared in the aliphatic series.

Electrolysis of Acetylacetone (Tetracetylethane). — Unlike malonic ether which in alcoholic solution is a non-conductor, a solution of acetylacetone in dilute alcohol is a true electrolyte, although not a very good one. This electrolysis therefore differs from the two preceding in that the positive ion is hydrogen instead of a metal.

Combes has shown[1] that acetylacetone possesses such strong acid properties that it is able to expel carbonic acid from all the metallic carbonates, thus proving itself a much stronger acid than acetoacetic ether. This fact, together with the interesting results obtained by Perkin in a recent study of the molecular magnetic rotation of acetyl acetone, render it highly probable that this substance is really an unsaturated alcohol in which the number of hydroxyl groups and double bondings present in any one molecule is to a certain extent dependent upon the temperature.[2] At the ordinary temperature, according to Perkin, the compound $\mathrm{CH_3 \atop OH}\!\!>\!\!C\!=\!CH.C\!\!<^{\!\!O}_{\!\!CH_3}$ predominates, and it is by the presence of such molecules, which are analogous in structure to the sodium compound of malonic ether, and might very naturally be dissociated to some extent in solution, that the formation of tetracetyl ethane as a product of the electrolysis of acetylacetone may be ascribed.

$$2{\mathrm{CH_3} \atop \mathrm{OH}}\!\!>\!\!C\!=\!CH.C\!\!<^{\!O}_{\mathrm{CH_3}}\!=H_2+ \begin{array}{l} \mathrm{CH_3 \atop OH}\!\!>\!\!C\!=\!C\!-\!C\!\!<^{\!O}_{\mathrm{CH_3}} \\ \mathrm{CH_3 \atop OH}\!\!>\!\!C\!=\!C\!-\!C\!\!<^{\!O}_{\mathrm{CH_3}} \end{array}$$
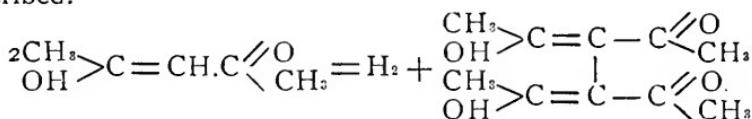
The above equation expresses what would be expected if the electrolysis of acetylacetone is a reaction that is strictly analogous to the two other reactions already described. The product would be a tetracetylethane that is at once alcohol and ketone, and which is isomeric with the tetraketone $(C_2H_3O)_2CH\!-\!CH(C_2H_3O)_2$, the compound that by a strict nomenclature should be called tetracetylethane.

40 grams of pure "acetylacetone" prepared by Claissen's method[2] were dissolved in 60 cc. of 50-per cent. alcohol and the solution

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[1] A. Combes: Compt. Rend. 105, 868.   [2] Perkin: Jour. Chem. Soc. 1892, 816.
[3] Ber. d. chem. Ges. 22, 1009.

distributed among three small electrolytic cells connected in parallel circuit. The electrolysis was continued for three weeks. The current which passed through all these cells during this period averaged about one-fifteenth of an ampère.

Hydrogen was continuously evolved at the cathode, and white crystalline scales were noticed at the bottom of one cell as early as the end of the first day. These crystals, although freely soluble in boiling alcohol, were very sparingly soluble in cold alcohol. Had the compound been more soluble in cold dilute alcohol its formation might have escaped observation. The crystals were removed from the cells every three or four days, until at the end of three weeks a new crop failing to appear, the electrolysis was discontinued. The crystals after being washed with dilute alcohol were found to melt at 189° (corrected). Repeated recrystallization from hot alcohol and benzene raised the melting-point to 191.2° (corrected). The crystals from benzene were well developed, colorless cubes. From 40 grams of acetylacetone only about 0.8 gram of pure crystals was obtained for analysis and further study.

Combustions with copper oxide gave the following figures :

I. 0.2041 gram substance gave 0.4528 gram CO_2 and 0.1298 gram H_2O.

II. 0.2094 gram substance gave 0.4614 gram CO_2 and 0.1326 gram H_2O.

III. 0.2088 gram substance gave 0.1329 gram H_2O.

	Calculated for $C_{10}H_{14}O_4$.	Found I.	Found II.	Found III.
C	60.61	60.50	60.10	...
H	7.07	7.07	7.03	7.07
O	32.32	32.43	32.87	...
	100.00	100.00	100.00	

The material used for the combustions had previously been employed for molecular-weight determinations in benzene solution in the Beckmann freezing-point apparatus. Tetracetylethane is so sparingly soluble in benzene that only two observations of the lowering of the freezing-point could be made in one series. The molecular weight calculated for $C_{10}H_{14}O_4$ is 198; that found was 183 and 184.

Like acetylacetone, tetracetylethane is a weak acid. It dissolves quickly and completely in solutions of alkaline hydroxides

and with some difficulty in alkaline carbonates. Stronger acids precipitate it from these alkaline solutions with its melting-point unchanged. A solution containing a drop of bromine in 5 cc. of chloroform was completely decolorized by 0.03 gram of tetracetyl-ethane in less than two minutes without exposure to direct sun-light. A trace of hydrobromic acid was formed, but the rapidity of the decolorization suggested the idea that the action was mainly one of addition rather than of simple substitution.

The principal product of the electrolysis of acetylacetone which remained in the cells after the removal of the crystals was a reddish-colored syrup of aromatic odor but of most unpromising appearance, from which no definite compounds have yet been isolated.

To prepare tetracetylethane in quantities sufficiently large to enable me to study its reactions more closely, I found myself forced to try the action of iodine on the sodium salt of acetyl acetone. 9.2 grams (1 atom) of fine sodium wire were placed in a flask containing absolute ether and connected with a return-cooler. 40 grams (1 molecule) of acetylacetone were then added, and the mixture well cooled. Hydrogen was evolved, and at the end of half an hour the sodium had been completely changed into white sodic acetylacetonate. 50.8 grams of iodine dissolved in dry ether were then slowly poured upon the mixture with constant shaking. When the reaction was ended the ether was distilled off and the sodium iodide dissolved out by water. The residue insoluble in water was tetracetylethane. It was purified by crystallization from boiling alcohol and melted at 191°. The yield was only 20 per cent. less than the theoretical.

A 1,4-diketonetetracetylethane should give several character-istic condensation-products. Thus, when its solution in glacial acetic acid is boiled with ammonium-acetate solution and then with dilute sulphuric acid and a pine-splinter—Knorr's pyrrol reaction—the splinter assumes a deep red color, showing that 1,4 dimethyl-2,3-diacetylpyrrol has been formed :

$$C_2H_3O—C——C—C_2H_3O \qquad\qquad C_2H_3O.C—C—C_2H_3O$$

$$\begin{array}{cc} \| & \| \\ COH & COH \\ | & | \\ CH_3 & CH_3 \end{array} \quad +NH_3=2H_2O+ \quad \begin{array}{cc} \| & \| \\ CH_3C & CCH_3 \\ & V \\ & NH \end{array}$$
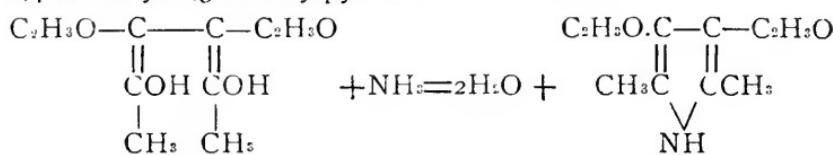
By an analogous condensation, in which one molecule of water is withdrawn from one molecule of tetracetylethane by concentrated

sulphuric acid, a quantitative yield of 1,4-dimethyl-2,3-diacetyl-furfuran may be obtained:

$$
\begin{array}{l}
\underset{\displaystyle\substack{\|\\ C(OH)(HO)C\\ |\\ CH_3 \quad\quad CH_3}}{C_2H_3O.C\text{————}C\text{—}C_2H_3O} \quad = H_2O + \quad \underset{\displaystyle\substack{\| \quad \|\\ CH_3.C \quad C\text{—}CH_3\\ \diagdown\diagup\\ O}}{C_2H_3O.C\text{—}C.C_2H_3O}
\end{array}
$$
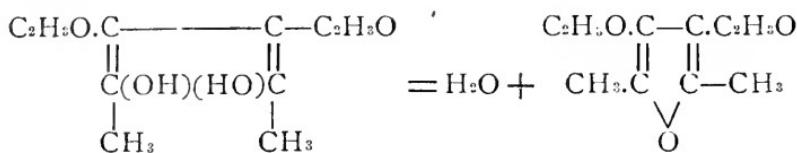
4 grams of tetracetylethane were dissolved in 7 cc. of cold concentrated sulphuric acid. Some heat was evolved. The solution, which was nearly colorless, was allowed to stand for ten minutes and then poured into about 50 cc. of cold water. The furfuran derivative soon crystallized out as a mass of pure white interlacing needles, weighing 3.5 grams. It dissolved readily in boiling water, and crystallized out, as the solution cooled, in long, silky needles having the appearance of glass-wool. When warm the body possesses a faint, agreeable aromatic odor. It melts at 63°. When analyzed it gave the following figures:

0.3273 gram substance gave 0.8008 gram CO_2 and 0.0214 gram H_2O.

	Calculated for $C_{10}H_{12}O_3$.	Found.
C	66.66	66.73
H	6.66	6.53
O	26.67	26.74

Electrolysis of Acetoacetic Ether (Diacetylsuccinic Ether).— As already stated, acetoacetic ether conducts the electric current slightly when dissolved in water; and in such a solution, if anywhere, one might expect that molecules containing the hydroxyl group and double bond would be present. On this assumption the following reaction might be anticipated:

$$
\begin{array}{l}
\underset{\displaystyle\substack{|\\ HC:C(OH).CH_3\\ |\\ HC:C(OH).CH_3\\ |\\ CO_2R}}{CO_2R} \quad = H_2 + \quad \underset{\displaystyle\substack{|\\ CH.CO.CH_3\\ |\\ CH.CO.CH_3\\ |\\ CO_2R}}{CO_2R} \quad .
\end{array}
$$
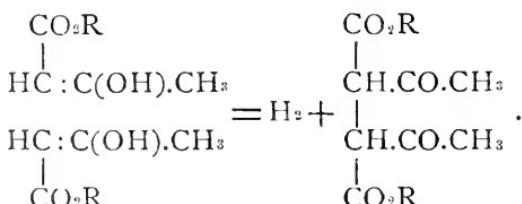
It will be remembered that it is by the action of iodine upon the sodium salt of acetoacetic ether that diacetylsuccinic ether is usually prepared. This compound was not actually isolated from

the other products formed during the electrolysis of acetoacetic ether, but its presence among them was proved without difficulty.

25 grams of acetoacetic ether were dissolved in twice their weight of 50-per cent. alcohol and a current of one-seventh of an ampère passed through the solution for several days. This treatment of the acetoacetic ether gave rise to a thick oil, which, like diacetyl-succinic ether, upon being boiled, first with ammonium-acetate solution and then with dilute sulphuric acid, according to Knorr's method, gave a faint pyrrol reaction with a pine-splinter. Judging from the depth of color imparted to the splinter, the quantity of diacetylsuccinic ether escaping decomposition during the electro-lysis must have been small. Later experiments made in this labora-tory by Mr. Weems showed that when concentrated aqueous solu-tions of the sodium salt of acetoacetic ether are electrolyzed under slightly different conditions, the yield of diacetylsuccinic ether may become relatively large.

The type of electrosyntheses illustrated in the preceding pages is an interesting one and demands further study. It is the inten-tion of the author to continue the investigation in the immediate future.

WORCESTER, MASS., *June*, 1893.

REVIEWS AND REPORTS.

The appearance at this time of the first two volumes of the new edition of Ostwald's famous *Lehrbuch* will enhance not a little the rapidly growing interest which has been aroused by the wonderful development during the past decade of all phases of the theory of chemical processes. Since the completion of the first edition, five years ago, the discoveries in general physical chemistry—in particular in the Theory of Solutions, electrochemistry, and the subject of Chemical Equilibrium—have been so extended and of such fundamental character as to make it necessary not only

entirely to rewrite the work, but nearly to double its size. The historical method of treatment, which was the charm of the earlier edition, is preserved in the new; the clearness and exhaustiveness with which the subjects are presented render the book most fascinating reading.

The first volume, the *Stoechiometrie*, takes up the mass-relations of chemical compounds, with a critical recapitulation of the determinations of atomic weights, and then devotes six chapters to the laws of gases and thirteen to the properties of liquids. The Theory of Solutions is presented as a separate subject, and is followed by an extended discussion of the properties of solids, the volume closing with the Periodic Law and the Molecular Theory.

An unusual measure of interest is excited by the succeeding volume—on Chemical Energy—for the reason that here, for the first time in the history of chemical theory, the general doctrine of energy is exhaustively developed and applied. Thermochemistry, electrochemistry and photochemistry are regarded as treating the transformations between chemical energy, on the one hand, and heat, electricity and radiant energy on the other. The substantiality of energy, its forms, its capacity- and intensity-factors, and the laws of its transformations, are brought out and emphasized; the significance of the intensity-factor of chemical energy—the chemical potential—in the theory of chemical equilibrium is made apparent; the history of the energy doctrine is outlined.

That thermodynamics is a special phase of the energy doctrine clearly appears from the chapters on thermochemistry. Here, in addition to the theory, are collected from the literature all reliable thermochemical data—a rather remarkable task in itself. The "book" on electrochemistry is a brilliant piece of work. The historical development—from Grotthuss to the free-ion theory; from Hittorf and Kohlrausch to Arrhenius and Ostwald—is most interesting, and is followed by complete discussion of the magnificent results in the theory of concentration-currents and of the voltaic cell, the whole treated from one point of view: as necessary deductions from the laws of energy. Many new conclusions are drawn and confirmed by experiment; the whole reads like an original paper and is inspiring in the extreme. The volume is concluded by a similar presentation of the facts and theories of photochemistry.

The final volume (Band II, zweiter Teil), which is to appear later this year, will treat of Chemical Equilibrium, the Law of Mass-action and the applications of thermodynamics—in short, all that is known as the *Verwandschaftslehre*. Its coming will be awaited with no little interest.   J. E. T.

AMERICAN

CHEMICAL JOURNAL.

THE METALLIC DERIVATIVES OF ACETYLENE.

By Edward H. Keiser.

In a previous paper [1] it was shown that the explosive compounds obtained by the action of acetylene upon ammoniacal solutions of cuprous chloride and silver nitrate have the composition represented by the formulas C_2Cu_2 and C_2Ag_2, and that they are to be regarded as metallic substitution-products of this hydrocarbon. The work upon the metallic derivatives of acetylene has been continued, and a study has now been made of the action of the hydrocarbon upon aqueous and alkaline solutions of mercuric salts. When acetylene acts upon cuprous and silver salts the compounds Cu_2C_2 and Ag_2C_2 are formed both in aqueous and ammoniacal solutions. In the case of the mercuric salts, however, the action is different in aqueous from what it is in alkaline solution. Thus, when acetylene is conducted into a water solution of corrosive sublimate, a white granular precipitate is obtained which when dry is not explosive, and which does not dissolve in dilute acids with the evolution of acetylene. On the other hand, if the acetylene is passed into an alkaline mercuric solution—for example, a solution of mercuric iodide in potassium iodide to which caustic potash has been added—then a white flocculent precipitate is obtained. This precipitate when dry is extremely explosive, and it dissolves in dilute hydrochloric acid with the evolution of acetylene. It is analogous in all its properties to the silver and copper compounds of acetylene, and like these it is a metallic substitution-

[1] This Journal **14**, 285.

product of the hydrocarbon. Its composition is represented by the formula C_2Hg. The compound formed in an aqueous solution of mercuric chloride contains chlorine. Its composition is perhaps best represented by the formula $C_2(HgCl)_2$, and it may be regarded as acetylene in which the two hydrogen atoms have been replaced by two univalent (HgCl) groups.

The only reference in chemical literature to the explosive mercury compound of acetylene appears to be an article by H. Bassett[1] in the Chemical News for 1869. This experimenter passed coal-gas through Nessler's reagent and obtained a considerable quantity of a bright yellow precipitate which, after drying, exploded slightly when heated. He obtained a purer substance by passing the products of the incomplete combustion of coal-gas through Nessler's solution. A precipitate of a pale yellow color was formed which exploded rather more violently than that first obtained. An analysis of the substance gave 70.24 per cent. mercury and 23.5 per cent. iodine. Bassett gave to it the formula $C_2HHgI + HgO$.

In my earlier experiments it was found that the acetylene obtained by the incomplete combustion of coal-gas is mixed with so many other substances that pure silver and copper derivatives could not be obtained from it. For the preparation of the mercury compound the acetylene was made by the action of alcoholic potash upon ethylene bromide. The gas after leaving the generating-flask was passed through a solution of alcoholic potash heated on a water-bath, then it passed through two wash-bottles containing absolute alcohol and one containing water, and finally it was led into a solution of mercuric iodide in potassium iodide to which caustic potash had been added. A white flocculent precipitate was soon formed in large quantity. This was separated from the liquid by filtration, and was washed repeatedly with distilled water. The compound was then dried in desiccators over sulphuric acid. It does not, however, give up all its water in this way. It is only by prolonged heating upon the water-bath that it can be obtained entirely free from water. When it is heated to a higher temperature in an air-bath the compound gradually decomposes, the color becomes dark, and a vapor having an odor like that of phosphuretted hydrogen is given off. Apparently this decomposition begins at about 100°. Heated rapidly to a

[1] Chemical News **19**, 28.

somewhat higher temperature the compound explodes with extreme violence, finely divided carbon and mercury remaining behind. The compound contains no iodine. An analysis of the air-dried substance gave 83.11 per cent. mercury. After drying another portion of the same substance upon the water-bath until constant weight was obtained, a determination of mercury gave 88.9 per cent. The analysis was made by dissolving the weighed substance in dilute hydrochloric acid, precipitating the mercury as sulphide with hydrogen sulphide, and weighing the precipitate in a Gooch crucible after it had been dried until a constant weight was obtained.

Per cent. of Hg calculated for $C_2Hg =$ 89.28.
Per cent. of Hg calculated for $C_2Hg_2 =$ 94.33.
Per cent. of Hg calculated for $(C_2H)_2Hg =$ 80.00.
Found 88.94, 88.42 and 89.14.

The analysis of the substance, therefore, as well as its properties indicates that it is a true metallic substitution-product of acetylene. The formula being C_2Hg, the compound is especially interesting because in it both hydrogen atoms of the hydrocarbon are replaced by a single atom of a metal. Like the copper and silver compounds it dissolves readily in hydrochloric acid with the evolution of acetylene. A solution of mercuric chloride is thus obtained. When treated with an alcoholic solution of iodine it unites with the iodine slowly at ordinary temperatures, more rapidly at the temperature of the water-bath. Di-iodo-acetylene, C_2I_2, is thus formed. This, after standing some time, polymerizes and crystalline plates separate from the alcoholic solution. These crystals melt at 187° and are probably hexiodobenzene,[1] C_6I_6. This substance will be analyzed and studied more fully as soon as a larger quantity of it has been prepared.

Kutscherow[2] has studied the action of the acetylene hydrocarbons upon an aqueous solution of mercuric salts. He found that these hydrocarbons form non-explosive white precipitates, from which acids liberate addition-products of the hydrocarbons and water. Thus from acetylene aldehyde can be obtained, from allylene, acetone, from the higher members other ketones. He has not made any analyses of the compounds which acetylene forms with mercuric salts, his work having been mainly upon the allylene compounds. Analyses of the compound formed from

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[1] See Baeyer: Ber. d. chem. Ges. **18**, 2276.   [2] Ber. d. chem. Ges. **17**, 13.

allylene and an aqueous solution of corrosive sublimate led him to give this substance the formula $3HgCl_2.3HgO.2C_3H_4$, and he assigns to it a very complicated constitutional formula.

To obtain the acetylene compound the hydrocarbon, prepared as described above, was passed into a cold saturated solution of mercuric chloride. The solution soon became milky, and after a time a white granular precipitate settled to the bottom of the vessel. Hydrochloric acid is formed by this reaction. After a time the precipitation stops, although some mercury still remains in solution. The compound cannot be formed by passing acetylene through a solution of mercuric chloride in absolute ether. The precipitate was removed from the acid solution by filtration. It was washed first with water, then with alcohol, and finally with ether to ensure the removal of all mercuric chloride. It was then dried in desiccators over sulphuric acid. The compound was found to be insoluble in alcohol and ether, and was not acted upon by dilute hydrochloric acid. *Aqua regia* and fuming nitric acid dissolve it. The compound does not explode on heating, but if some of the dried substance be cautiously heated on a platinum spatula at a certain temperature it suddenly puffs up, forming a black porous mass, and white vapors are given off. If it is heated in a tube closed at one end a white sublimate of calomel, $HgCl$, is obtained and a porous mass of carbon remains behind. Like the explosive mercury acetylide this compound still retains some water after it has stood for a long time in the desiccator, and it is difficult to dry it in an air-bath without bringing about decomposition. Analyses of the compound after it had been dried in the desiccator gave results that agree fairly well with the formula $C_2(HgCl)_2.\frac{1}{2}H_2O$.

	Calculated.	Found.		
Hg	79.37	79.32	79.44	79.27
Cl	14.07	...	14.51	14.61
C	4.70	...	...	...
H₂O	1.86	...	1.63	1.74
	100.00			

Like the explosive mercury compound this one also unites with iodine, and from quantitative determinations one molecule of $C_2Hg_2Cl_2$ requires four atoms of iodine. This, taken in connection with the fact that, on heating, the compound is easily con-

verted into mercurous chloride and carbon, makes it seem probable that it is derived from acetylene by the replacement of the two hydrogen atoms by two HgCl groups. The equation of formation would then be:

$$C_2H_2 + 2HgCl_2 = 2HCl + C_2(HgCl)_2.$$
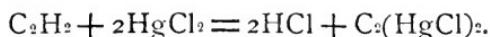
It is possible, however, that, when acetylene acts upon mercuric chloride, the compound C_2Hg is first formed, and that this unites immediately with a molecule of mercuric chloride, giving $C_2Hg_2Cl_2$.

The investigation of these and other metallic derivatives of acetylene will be continued.

In conclusion I desire to thank Miss E. H. Parker for valuable assistance given to me in making the experiments described in this paper.

Bryn Mawr, Pa., *June*, 1893.

VIII.—ON THE NITRITES OF SOME AMINES.

By W. A. Noyes.

Some time since it was shown[1] that dibenzyl-carbinamine forms a nitrite which is stable in its aqueous solution at ordinary temperatures. A number of other amines have now been prepared for the purpose of studying the stability of their nitrites. The experiments to be described establish pretty conclusively that amines of the general formula $\dfrac{R}{R}{>}CHNH_2$ form nitrites which are stable at ordinary temperatures. No amine of this type has been found, however, which is not decomposed on boiling the concentrated aqueous solution of its nitrite. On the other hand it has been found that hexamethylene-diamine (1-4-diamino-cyclo-hexane) is not so stable toward nitrous acid as was formerly supposed; also that the nitrite of dihydro-meso-anthramine decomposes quite easily on boiling with water. It is worthy of note, also, that Semmler[2] has found that β-methyl-penta-methylene-amine (1-3-methyl-amino-cyclo-pentane) reacts normally toward nitrous acid,

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[1] This Journal **14**, 225.   [2] Ber. d. chem. Ges. **25**, 3519.

giving the corresponding alcohol. Wislicenus and König[1] have recently obtained oxyhydrinden, $C_6H_4 \begin{matrix} CH_2 \\ \diagdown \\ CH-OH \end{matrix} \diagup CH_2$, by heating the chloride of amino-hydrindene with a solution of sodium nitrite.

Bamberger has recently expressed,[2] with some reserve, the opinion that the chemical character of completely hydrogenated ring systems is not dependent on the number of atoms included in the ring. If this be true, it must follow that, in their conduct toward nitrous acid, at least, there is no essential difference between alicyclic and aliphatic amines. The hydrogenated naphtyl amines studied by Bamberger and his co-workers are simply extreme cases, and the stability of their nitrites is not conditioned by the hydrogenated *ring*. Indeed Bamberger states that 1-2 phenyl-amino ethane[3] forms a nitrite which can be crystallized from boiling water. Apparently the chief factor in producing the strongly basic character of these amines and the stability of their nitrites is not the ring structure at all, but the accumulation of hydrogen in parts of the molecule which are in close proximity to the amine group.

Diethyl-carbinamine (*3-amino-pentane*).[4]

Diethyl-ketoxim was prepared by the method used by Scholl,[5] except that no alcohol was used. The diethyl-ketone with the solution of hydroxylamine chloride and sodium hydroxide were placed in a bottle and agitated for an hour by means of a turbine. The oxim was then removed from the solution with the aid of a little ether, the ethereal solution dried with calcium chloride and distilled till the thermometer rose to 150°. The portion remaining in the bulb was apparently the nearly pure oxim, and was reduced to the amine by means of absolute alcohol and sodium. The amine obtained was distilled from the alkaline solution in a current of steam ; the distillate was collected in dilute hydrochloric acid and the solution evaporated to dryness. The conversion into the oxim and reduction to the amine appear to be nearly quantitative. This method of preparing amines seems to be of quite

[1] Ann. Chem. (Liebig) **275,** 350.

[2] Ber. d. chem. Ges. **26,** 1286.

[3] Ann. Chem (Liebig) **257,** 19. The name given the compound by Dr. Bamberger would apply equally to the secondary amine derived from aniline.

[4] Communicated to the Chemical Section of the American Association for the Advancement of Science at the Rochester meeting.

[5] Ber. d. chem. Ges. **21,** 509.

general application, and for many cases it is better than any of the other methods in common use.

The crude chloride of the new base was decomposed with a strong solution of sodium hydroxide, the amine was taken up with ether, the ethereal solution was dried with stick potash and then with metallic sodium, and was submitted to fractional distillation.

Diethyl-carbinamine, $\dfrac{C_2H_5}{C_2H_5}$>$CHNH_2$, boils at 89°–91°. It is a colorless, mobile liquid with a penetrating, ammoniacal odor. It absorbs carbon dioxide greedily from the air, and a few drops left for some time in a loosely-stoppered test-tube were converted into well-formed, needle-shaped crystals. These are permanent in the air. The base is miscible with water in all proportions. Considerable heat is evolved when it is mixed with a small amount of water.

The specific gravity of the base is $D\dfrac{20°}{4°} = 0.7487$.

I. 0.1496 gram of the base gave 0.3796 gram CO_2 and 0.2042 gram H_2O.

II. 0.1433 gram of the base gave 0.3625 gram CO_2 and 0.1987 gram H_2O.

	Calculated for $\frac{C_2H_5}{C_2H_5}$>$CHNH_2$.	Found. I.	II.
C	68.97	69.20	68.97
H	14.94	15.17	15.41

The *chloride,* $C_5H_{11}NH_2.HCl$, is very easily soluble in water and in alcohol. It crystallizes from a concentrated aqueous solution in needles which are not deliquescent and which melt at 216°–217°.

0.0965 gram of the salt dried at 135° gave 0.1111 gram AgCl.

	Calculated for $C_6H_{11}NH_2.HCl$.	Found.
Cl	28.75	28.48

The *chloroplatinate* crystallizes in needles which are very easily soluble in water and in alcohol.

The *nitrite* can be prepared by passing nitrous anhydride into a solution of the base in dry ether. The salt separates in the form of white needles. If the ether is moist, a concentrated solution of the nitrite separates. The crystallized salt can be readily obtained by evaporating the aqueous solution over sulphuric acid *in vacuo.*

The salt is extremely deliquescent. At ordinary temperatures both the dry salt and its concentrated solution appear to be entirely stable. The dilute solution (1 : 2000) can be heated to boiling for some time without appreciable decompos 'ion, as was shown by quantitative color reactions with meta-phenylene-diamine. Evaporation to dryness causes an almost complete decomposition of the salt.

Dipropyl-carbinamine (4-amino-heptane).

Dipropyl-ketone was prepared by distilling normal calcium butyrate. The ketone was converted into the oxim and amine by methods similar to those used for diethyl-ketone. Dipropyl-carbinamine, $\frac{CH_3CH_2CH_2}{CH_3CH_2CH_2}{>}CHNH_2$, is a colorless, mobile liquid with an ammoniacal odor. It is but very slightly soluble in water. It boils at 139°–140°. The base absorbs carbon dioxide rapidly from the air, forming a carbonate which crystallizes in needles and which is very difficultly soluble in water. It dissolves more easily than the free base, however, as its solution becomes turbid on the addition of sodium hydroxide.

The specific gravity of the base is $D\frac{20°}{4°}=0.7667$.

0.1901 gram of the base gave 0.5033 gram CO_2 and 0.2520 gram H_2O.

	Calculated for $\frac{C_3H_7}{C_3H_7}{>}CHNH_2$.	Found.
C	73.04	72.20
H	14.78	14.73

The *chloride*, $C_7H_{15}NH_2.HCl$, is easily soluble in water and alcohol. It melts at 241°–242°. It crystallizes in needles.

0.1090 gram of the chloride gave 0.1036 gram $AgCl$.

	Calculated for $C_7H_{15}NH_2.HCl$.	Found.
Cl	23.43	23.49

The *chloroplatinate* separates in light yellow-colored scales which are difficultly soluble in water, more easily soluble in alcohol.

The *nitrite* is very easily soluble in water. When a little more than the calculated amount of a strong solution of sodium nitrite is added to the chloride nothing separates and no decomposition takes

place in the cold solution. When the solution is heated in boiling water for three-fourths of an hour, about 80 per cent. of the theoretical amount of nitrogen is evolved. It is noticeable that in this and in other similar cases the decomposition takes place rapidly in a concentrated solution, while it is much slower in a dilute solution, and with a certain degree of dilution appears to cease altogether. Kastle has observed a similar conduct on the part of silver chloracetate.[1] In the light of the theory of electrolytic dissociation it seems probable that the molecules which have become dissociated by dilution will no longer decompose in the ordinary manner.[2] It has recently been shown[3] that even ammonium nitrite becomes comparatively stable in dilute solutions, apparently for the same reason.

Di-isobutyl-carbinamine (2-6-dimethyl-4-amino-heptane).

Valerone was prepared from isovaleryl chloride (b. p. 115°–117.5°) by treatment with anhydrous ferric chloride by the method of Hamonet.[4] The yield was very poor. From 84 grams of valeryl chloride only 4 grams of valerone, boiling at 168°–172°, were obtained. Schmidt[5] gives the boiling-point of valerone as 181°–182°. Hamonet,[6] however, found the boiling-point 165°–167°, but thinks that his preparation was not pure. Schmidt prepared his valerone by distilling calcium valerianate, and obtained a yield of only 10 per cent. of the crude distillate. While the yield by Hamonet's method is no better, a consideration of the boiling-points of related compounds makes it probable that the valerone prepared by Schmidt was the normal compound (5-nonanone), while that obtained by Hamonet and myself was the isovalerone (2-6-dimethyl-4-heptanone). The boiling-point of the base given below, as the latter was prepared from a crystallized chloride, is probably more trustworthy than that of the valerone. That boiling-point indicates that the true boiling-point of isovalerone must be about 170°, since with increasing molecular weight the boiling-point of the amine approaches that of the corresponding ketone.

The valerone (4 grams) was converted into the oxim by heating on the water-bath for two hours with hydroxylamine chloride (4

[1] This Journal **14**, 586.   [2] See Ostwald: Zeit. f. phys. Ch. **11**, 431.
[3] Anzeli and Boeris: Gazz. Chim. **22**, 2, 349.   [4] Ber. d. chem. Ges. **22**, R. 766.
[5] *Ibid.* **5**, 600.   [6] Bull. Soc. Chim. (3) **2**, 334–347.

grams), caustic soda (2 grams), water (12 cc.) and alcohol (10 cc.). The oxim was taken up with ether, the solution washed twice with water to free it from alcohol, dried with calcium chloride, and the ether distilled off. The oxim remaining was reduced as usual. The chloride of the base obtained was crystallized from water, and the base separated from the chloride was dried with stick potash and metallic sodium.

Di-isobutyl-carbinamine is a colorless liquid with a strong ammoniacal odor. It boils at 166°–167°. It is almost insoluble in water, and caustic soda produces a turbidity even in very dilute solutions of the chloride. The specific gravity is $D\frac{20°}{4°} = 0.772$.

I. 0.1394 gram of the base gave 0.3808 gram CO_2 and 0.1830 gram H_2O.

II. 0.2251 gram of the base gave 0.6171 gram CO_2 and 0.2950 gram H_2O.

	Calculated for $\begin{array}{c}(CH_3)_2.CH.CH_2\\(CH_3)_2.CH.CH_2\end{array}{>}CHNH_2.$	Found. I.	II.
C	75.52	74.51	74.77
H	14.69	14.58	14.57

The chloride, $C_9H_{19}NH_2.HCl$, crystallizes in needles which are moderately soluble in water. These melt at 247°–248° without apparent decomposition.

0.1107 gram of the chloride gave 0.0886 gram AgCl.

	Calculated for $C_9H_{19}NH_2HCl$.	Found.
Cl	19.78	19.79

The *chloroplatinate* consists of fine needles of a light yellow color. These are almost insoluble in water.

The *carbonate* forms rapidly in white needles when the base is exposed to the air. These are almost insoluble in water, easily soluble in alcohol.

The *nitrite* is precipitated in the form of white, fine needles, easily soluble in water when a strong solution of sodium nitrite is added to a strong solution of the chloride. About 79 per cent. of the theoretical amount of nitrogen was evolved when the chloride was heated for a short time on the water-bath with a little more than the calculated amount of sodium nitrite.

When nitrous anhydride is passed into an ethereal solution of

the base a crystalline salt is precipitated. When a solution of the salt obtained in this way is evaporated on the water-bath a crystalline residue remains, which gives qualitative tests for nitrous acid. A quantitative examination, however, shows that the nitrite has been largely decomposed. As an exactly similar test was relied on to establish the stability of the nitrite of hexamethylene-diamine,[1] it was thought best to test the conduct of that body once more.

Hexamethylene-diamine (*1-4-diamino-cyclo-hexane*).

A small portion of a chloride of the base remaining from a previous preparation[2] was recrystallized from water and washed with strong alcohol, in which it is very difficultly soluble. An analysis of the purified chloride gave 37.49 per cent. of chlorine. Theory requires 37.97 per cent. When this chloride was heated on the water-bath for half an hour with a little more than the calculated amount of sodium nitrite, about 23 per cent. of the theoretical amount of nitrogen was evolved, or a little less than one atom of nitrogen for one molecule of the base. While it is certain that some decomposition takes place, it does not appear to occur in the normal manner. I hope to make a further study of the matter, and especially of the products of decomposition.

Dihydro-meso-anthramine.

Meso-anthramine was prepared from anthranol by heating it in sealed tubes with strong aqua ammonia.[3] It was reduced to the dihydro compound by means of alcohol and sodium. There was some evolution of ammonia during the reduction, showing the strong tendency of the base to be converted into anthracene by the loss of ammonia.[4]

The chloride of the base when treated with a strong solution of sodium nitrite in the cold suffers no decomposition, but on boiling for a short time about 79 per cent. of the theoretical amount of nitrogen is evolved. The main product of the decomposition is anthracene.

Diphenyl-carbinamine (*Benzhydrylamine*).[5]

The amine was prepared by the reduction of the oxim by means of alcohol and sodium. This method seems better than the one

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[1] Baeyer and Noyes: Ber. d. chem. Ges. **22**, 2172.   [2] *Loc. cit.*

[3] Goldmann: Ber. d. chem. Ges. **23**, 2522.   [4] *Ibid.* **23**, 2526.

[5] I am indebted to Mr. E. Brown for the preparation of this amine.

used by Goldschmidt.[1] When a strong solution of sodium nitrite is added to a solution of the chloride of the base the nitrite separates in well-formed needles which are somewhat difficultly soluble in water. A quantitative colorimetric determination of nitrous acid in these needles showed that they consisted of the pure nitrite. Both the needles and their aqueous solution appear to be perfectly stable at ordinary temperatures. When the concentrated solution of the nitrite is heated in the water-bath for half an hour about 83 per cent. of the theoretical amount of nitrogen is evolved. Diphenyl-carbinol appears to be the main product of the decomposition.

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NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.

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In the present paper I have brought forward a number of observations and analyses which I hope will be of service to those who are engaged in the study of the rarer earths. The subject is one of such extreme difficulty, that even the results of an imperfect study may have value.

For the material which I have employed I have been chiefly indebted to Dr. Waldron Shapleigh, Chemist to the Welsbach Incandescent Light Company, by whom I have been liberally supplied with various preparations in a state of considerable purity. I have also to make my acknowledgments to Professor Everhart, from whom I have received a considerable quantity of gadolinite from the well known locality in Llano County, Texas. The material given me by Dr. Shapleigh consisted in part of beautiful crystalline double nitrates of the earths and ammonium, and in part of crude oxides. The double nitrates contained only the earths present in cerite, and for the most part only Ce_2O_3, Ln_2O_3, Ps_2O_3, and Nd_2O_3, with very small relative quantities of

[1] Ber. d. chem. Ges. **19**, 3233.

Y_2O_3, and traces only of other earths. In converting the crude oxides into sulphates it is best to sift the fine powder slowly upon the surface of cold dilute sulphuric acid. The sulphates are then formed at once as fine crystalline powders free from hard lumps. Another method sometimes applicable with advantage consists in mixing the oxides with an excess of ammonic sulphate, and then igniting slowly in porcelain crucibles, which are to be heated in a muffle to low redness until vapors are no longer given off. The sulphates then present a beautiful snow-white soft crystalline powder, and readily form saturated solutions with cold water. In all work with the rare earths, oxalates from their insolubility play a very important part. They may, as all chemists know, be readily converted into sulphates by treatment with sulphuric acid and careful expulsion of the excess of this last by heat. I have found it more convenient to mix the oxalate intimately with an excess of ammonic sulphate and heat carefully in a muffle, as in the last case. The resulting sulphates are perfectly soluble without packing together if sifted upon the surface of cold water. They are also perfectly neutral. The oxalates may also be converted into chlorides by mixing them intimately with ammonic chloride and igniting the mixture in a muffle very gently.

Determinations of mean atomic mass are now always employed in the study of the mixtures of oxides which present themselves in the attempt to effect separations. Very accurate results are obtained by the usual method of converting a weighed quantity of oxides into the equivalent weight of sulphates by treatment with sulphuric acid and subsequent careful ignition. Probably this could be done more conveniently, and in less time, by igniting the oxides in porcelain crucibles in a muffle, after mixing carefully with ammonic sulphate, but upon this point I have made no quantitative experiments.

In all my work I have employed the analysis of the oxalates as convenient and accurate. It is, however, necessary to insist upon several points of detail. In the first place I remark that the preparation of perfectly homogeneous mixtures of the oxalates requires much care. It is best to precipitate by a hot dilute solution of oxalic acid added slowly in small but distinct excess to a hot dilute solution of the mixed chlorides or nitrates. The precipitated oxalates are then to be thoroughly washed by decantation with hot distilled water. This requires in general a large quantity of water, and must be continued until the washings contain no trace

of oxalic acid and give no cloudiness with ammonia. Auer von Welsbach's process, which consists in adding a very dilute solution of the nitrates (or chlorides) to a hot dilute solution of oxalic acid, gives the oxalates in a state of very fine subdivision and perfectly free from hard masses. The mixed washings on saturation with ammonia sometimes give a precipitate of oxalates, though in small quantity. These oxalates may be washed and mixed with the main portion. The mass is to be dried upon a water-bath, and then thoroughly mixed in a dry mortar. Only in this manner is it possible to obtain a mass of oxalates sufficiently homogeneous to yield corresponding results when different portions are analyzed. The determination of the mean atomic mass in the oxalates prepared as above involves only the determination of the percentages of oxide R_2O_3 and of C_2O_3, the water present being of course without influence. Here I may remark that, as has doubtless been observed by other chemists, the last portions of water require a very high temperature for expulsion. The details of the method which I employ are as follows: From 0.5 gram to 1 gram of the oxalate is to be gently heated until the greater part of the water and carbonic dioxide have been driven off, and then at a full red heat for fifteen to twenty minutes with a blast lamp to a constant weight. During ignition the crucible is best placed at an angle, and partly uncovered to permit free access of air. The mixed oxides do not retain a weighable amount of carbonic dioxide. To determine C_2O_3, from 0.3 gram to 0.4 gram of the oxalate are to be weighed into a 250-cc. flask ; 20 cc. of water and 30 cc. of dilute sulphuric acid, 1 : 6 by volume, are then to be added and the flask is to be gently heated upon a sand-bath until the solution is complete, when the hot liquid is to be titrated with carefully standardized permanganate. The following analyses will show the correspondence between the results obtained by the above described method and those obtained by the sulphate process. In an oxalate from a perfectly colorless nitrate of lanthanum and ammonium sent me by Dr. Shapleigh,—

(1) 0.3344 gram gave 0.1009 gram C_2O_3 = 30.15 per cent.
(2) 0.3274 gram gave 0.09895 gram C_2O_3 = 30.07
(3) 0.3726 gram gave 0.1120 gram C_2O_3 = 30.08
(4) 0.3485 gram gave 0.1050 gram C_2O_3 = 30.11
(5) 0.5931 gram gave 0.2706 gram R_2O_3 = 45.61
(6) 0.5977 gram gave 0.2728 gram R_2O_3 = 45.64

The means are 30.10 per cent. C_2O_3, and 45.625 per cent. R_2O_3. The mean atomic mass calculated from the above is 139.70. Dr. Shapleigh found by the sulphate method 139.75, 139.72, 139.67, mean 139.71.

The necessity of thoroughly mixing the oxalates will appear from the following analyses made with oxalates simply washed and dried:

(7) 0.3549 gram gave 0.1274 gram $C_2O_3 = 35.88$ per cent.
(8) 0.3697 gram gave 0.1316 gram $C_2O_3 = 35.59$
(9) 0.3807 gram gave 0.1382 gram $C_2O_3 = 36.29$
(10) 0.6550 gram gave 0.2869 gram $R_2O_3 = 43.79$
(11) 0.6125 gram gave 0.2699 gram $R_2O_3 = 44.07$

The same oxalates carefully mixed in a mortar were also analyzed for comparison:

(12) 0.3357 gram gave 0.1213 gram $C_2O_3 = 36.16$ per cent.
(13) 0.3856 gram gave 0.1393 gram $C_2O_3 = 36.13$
(14) 0.6538 gram gave 0.2906 gram $R_2O_3 = 44.45$
(15) 0.7074 gram gave 0.3145 gram $R_2O_3 = 44.46$

The analyses leave no doubt whatever as to the necessity of carefully mixing the precipitated oxalates. They also show that in determinations of atomic mass by the sulphate method both oxalates and oxides should be well ground up to secure homogeneity. It has been shown that the oxalate and sulphate methods executed with proper care give equally accurate results. Each has its advantages, and in this respect there is but little choice. As the study of the rarer earths as now conducted usually depends more or less upon the properties of the double salts which they form with potassic and sodic sulphates, it may be well to call attention to facts not, I believe, noticed in printed papers, though doubtless recognized. The first is that the earths in the double sulphates may be converted directly into oxalates by boiling the sulphates with chlorhydric and oxalic acids, and then diluting with much water. The second fact is that oxalates obtained in this way, as from any alkaline solutions, should always be converted into oxides by ignition. These should then be dissolved in chlorhydric acid, again precipitated by oxalic acid, and the oxalates thoroughly washed.

In determining atomic masses by either the sulphate or oxalate method, the assumption is tacitly made that all the oxides taken

for analysis are of the type R_2O_3. This is not true when cerium is present, as in that case a portion at least of this metal is present as CeO_2 after ignition. Higher oxides than R_2O_3 are also present to some extent, at least when praseodymia and neodymia are mixed with ceria, or even when this last oxide is absent. Ceric oxide is not reduced by a full red heat to cerous oxide, or even by a current of hydrogen, at least in a crucible. The error committed is not, however, large when we consider the cerium as Ce_2O_3 instead of Ce_2O_4, and is still less in the cases of the other oxides. When great accuracy is necessary, it may be well to remove the four cerite oxides by means of potassic or sodic sulphate before determining the atomic mass.

In a number of analyses I determined the percentage of oxides by simply igniting the oxalate with a weighed quantity of pure sodic tungstate. This method gives very accurate results, but, as pure sodic tungstate must always be specially prepared in the laboratory, is not to be greatly recommended. Ceric oxide is not reduced to cerous oxide by heating with the tungstate to a red heat for some time. I may here state that a test for ceria more delicate than that which I gave many years since (PbO_2 and NO_3H) is obtained by employing the oxide of bismuth, Bi_2O_4, in place of plumbic oxide.

With these preliminaries I proceed to special methods of separating the mixed oxides. A series of experiments was first made to determine to what extent differentiation is effected by successive partial precipitations by oxalic acid. The method is of course not new, but, so far as I know, it has not been tested by quantitative analyses, and no attempt has been made to determine the rate of change. The material used in this case was a mixture of sulphates, the sulphate of neodymium being present in largest quantity. Thoric and other oxides in less quantity were also present. The material was obtained from Dr. Shapleigh in the form of oxides. After careful purification the atomic mass of the oxides was first determined:

(16) 0.5622 gram gave 0.1715 gram $C_2O_3 = 30.50$ per cent.
(17) 0.4782 gram gave 0.1458 gram $C_2O_3 = 30.50$
(18) 0.4355 gram gave 0.1326 gram $C_2O_3 = 30.47$
(19) 0.6100 gram gave 0.2778 gram $R_2O_3 = 45.55$
(20) 0.6904 gram gave 0.3141 gram $R_2O_3 = 45.50$

The analyses give as the atomic mass 137.25. A portion of the oxides was then converted into sulphates, and the number of cubic centimeters of a solution of oxalic acid required for complete precipitation determined by experiment with a sufficiently close approximation. A solution of the sulphates having a very fine rose-red color was then precipitated in five successive additions of equal volumes of a solution of oxalic acid. After each addition of the acid the resulting oxalate was filtered off and washed. The washings were then added to the filtrate. It will be seen that in this way the bulk of the solution increased before each precipitation after the first. The results are as follows:

I. (21) 0.3126 gram gave 0.0941 gram C_2O_3＝30.52 per cent.
　(22) 0.3410 gram gave 0.1042 gram C_2O_3＝30.54
　(23) 0.5773 gram gave 0.2820 gram R_2O_3＝48.84
　(24) 0.5856 gram gave 0.2855 gram R_2O_3＝48.75
　　　　Atomic mass 148.60.

II. (25) 0.3563 gram gave 0.1114 gram C_2O_3＝31.26
　(26) 0.3500 gram gave 0.1091 gram C_2O_3＝31.20
　(27) 0.6848 gram gave 0 3317 gram R_2O_3＝48.43
　(28) 0.6664 gram gave 0.3223 gram R_2O_3＝48.37
　　　　Atomic mass 143.35.

III. (29) 0.3500 gram gave 0.1113 gram C_2O_3＝31.78
　(30) 0.3127 gram gave 0.09936 gram C_2O_3＝31.77
　(31) 0.6859 gram gave 0.3345 gram R_2O_3＝48.75
　(32) 0.7087 gram gave 0.3447 gram R_2O_3＝48.65
　　　　Atomic mass 141.55.

IV. (33) 0.3350 gram gave 0.1042 gram C_2O_3＝31.12
　(34) 0.3410 gram gave 0.1060 gram C_2O_3＝31.09
　(35) 0.6369 gram gave 0.2958 gram R_2O_3＝46.44
　(36) 0.6468 gram gave 0.3004 gram R_2O_3＝46.45
　　　　Atomic mass 137.25.

V. (37) 0.2042 gram gave 0.06864 gram C_2O_3＝33.62
　(38) 0.2031 gram gave 0.06828 gram C_2O_3＝33.62
　(39) 0.3045 gram gave 0.1409 gram R_2O_3＝46.26
　(40) 0.3400 gram gave 0.1569 gram R_2O_3＝46.14
　　　　Atomic mass 124.40.

The filtrate from the last portion of oxalates contained only traces of earths. The analyses show that the earths with the high-

est atomic masses are precipitated first by oxalic acid. The average rate of decrease of mean atomic mass is five units for each operation, but the rate is by no means uniform. The results prove that precipitated oxalates must be very carefully mixed mechanically before analysis when more than one earth is present. The analyses also show that four-fifths of the earths might have been precipitated at once by oxalic acid if the object had been to obtain yttria with the least outlay of time and labor, the atomic mass of the last fifth being 124.40.

Oxychlorides.—When the chlorides of the metals belonging to the cerium and yttrium groups, or more generally stated, of the metals yielding the rarer earths, are carefully heated, oxychlorides are formed in greater or less proportion mixed with undecomposed chlorides. We may distinguish these as acid and basic chlorides. Water dissolves out the former very readily and leaves nearly or quite colorless basic chlorides, which are, relatively at least, insoluble. I find that in this way the earths present are separated into two groups, and that by repeating the operation upon each group a second differentiation is effected in each case. The process appears to deserve attention, and to compare very favorably with separation by means of basic nitrates. The details of this method are as follows :

The mixed oxides in as pure a state as possible are to be dissolved in a small excess of pure chlorhydric acid ; the solution is then to be evaporated at first on a water-bath, and then on a sand-bath, until a thick syrup is obtained. This is to be transferred to a porcelain crucible, which is then to be heated gently in a muffle. The heat should not be allowed to exceed low redness. Much chlorhydric acid is given off during the heating, and a white mass remains which consists in part of a mixture of oxychlorides, and in part of unaltered chlorides. The mass is then to be treated with hot water in rather small portions at a time, the solution being poured off before each new addition. When the washing is nearly complete, the solution becomes turbid. The white insoluble mass and supernatant liquid are then to be evaporated to dryness, or to a thick syrup, after the addition of enough chlorhydric acid to effect complete solution. The liquid poured off and containing the soluble chlorides is also to be evaporated to dryness, but without addition of chlorhydric acid. We have then two separate portions, of which one, A, contains the soluble

or relatively acid chlorides, and the other, B, the neutralized oxychlorides. Each of these portions is to be treated in the muffle, as in the first case. In this manner two new basic chlorides, B_2 and B_3, and two new acid chlorides, A_2 and A_3, are obtained. The same processes are to be repeated as long as the material lasts. The atomic mass of the oxides taken must first be determined, and afterward the atomic masses of the portions A_1, A_2, A_3, etc., and B_1, B_2, B_3, etc. This enables us to determine the rate of change in the atomic masses produced by the successive operations. Of course, it is only necessary to take a small portion of each product A_1, B_1, etc., for the determination of the atomic mass. The whole process will perhaps be rendered more clear by means of a diagram, and in illustration I shall select the results of actual work in a particular case. The starting-point in this case was a mixture of oxides from Texas gadolinite having the atomic mass 107.5. The data are as follows:

(41) 0.3577 gram gave 0.1357 gram $C_2O_3 = 37.94$ per cent.
(42) 0.3246 gram gave 0.1228 gram $C_2O_3 = 37.81$
(43) 0.3999 gram gave 0.1515 gram $C_2O_3 = 37.86$
(44) 0.6113 gram gave 0.2814 gram $R_2O_3 = 46.04$
(45) 0.6670 gram gave 0.3064 gram $R_2O_3 = 45.94$
(46) 0.6303 gram gave 0.2892 gram $R_2O_3 = 45.88$
     Atomic mass 107.5.

     B_1 Left. Atomic mass 110.8.
(47) 0.6836 gram gave 0.3289 gram $R_2O_3 = 48.11$ per cent.
(48) 0.2344 gram gave 0.0904 gram $C_2O_3 = 38.57$

     A_1 Right. Atomic mass 94.75.
(49) 1.2740 grams gave 0.4976 gram $R_2O_3 = 39.65$ per cent.
(50) 0.2998 gram gave 0.1065 gram $C_2O_3 = 35.51$

     B_2 Left. Atomic mass 117.4.
(51) 0.4327 gram gave 0.2157 gram $R_2O_3 = 49.84$ per cent.
(52) 0.2860 gram gave 0.1089 gram $C_2O_3 = 38.07$

     A_2 Left. Atomic mass 98.35.
(53) 0.7897 gram gave 0.3714 gram $R_2O_3 = 47.03$ per cent.
(54) 0.3772 gram gave 0.1566 gram $C_2O_3 = 41.52$

     B_3 Left. Atomic mass 122.
(55) 0.5910 gram gave 0.2803 gram $R_2O_3 = 47.43$ per cent.
(56) 0.2023 gram gave 0.0710 gram $C_2O_3 = 35.09$

A₃ Left.   Atomic mass 102.8.

(57) 0.4472 gram gave 0.2137 gram $R_2O_3 = 47.78$ per cent.

(58) 0.3067 gram gave 0.1248 gram $C_2O_3 = 40.70$

A₁ Right.   Atomic mass 94.75.

(59) 1.2740 grams gave 0.4976 gram $R_2O_3 = 39.05$ per cent.

(60) 0.2998 gram gave 0.1065 gram $C_2O_3 = 35.51$

A₂ Right.   Atomic mass 91.65.

(61) 1.0032 grams gave 0.3948 gram $R_2O_3 = 39.37$ per cent.

(62) 0.5057 gram gave 0.1856 gram $C_2O_3 = 36.77$

B₂ Right.   Atomic mass 98.6.

(63) 0.7353 gram gave 0.3291 gram $R_2O_3 = 44.75$ per cent.

(64) 0.3343 gram gave 0.1318 gram $C_2O_3 = 39.43$

A₃ Right.   Atomic mass 89.5.

(65) 0.4864 gram gave 0.2146 gram $R_2O_3 = 44.12$ per cent.

(66) 0.2212 gram gave 0.0929 gram $C_2O_3 = 42.00$

B₃ Right.   Atomic mass 92.35.

(67) 0.5183 gram gave 0.2238 gram $R_2O_3 = 43.17$ per cent.

(68) 0.2080 gram gave 0.0834 gram $C_2O_3 = 40.07$

The following diagram enables us to take in all the results at a glance.

It must be noted that in the above and on the diagram, B₁, B₂, B₃, etc., denote basic or oxychlorides; A₁, A₂, A₃, etc., neutral or relatively acid chlorides.   The analyses were not pursued further

because the material taken was exhausted by the separations accomplished. The examination of the results obtained in this particular case by the basic-chloride process leads to interesting conclusions. In the first place, it will be remarked that the atomic masses of the insoluble basic chlorides increase with each successive separation into basic and acid chlorides, while the neutral or relatively acid chlorides give diminishing atomic masses. In the cases of these last, three successive operations give a nearly pure yttria, with atomic mass 89.5. The rate of increase of the atomic masses of the successive portions B_1, B_2, B_3, is about 5.3 units for each operation. The rate of decrease of the portions A_1, A_2, A_3, is about 2.6 units for each operation. It is not to be expected that perfectly uniform results will be obtained even when the process is applied to the same mixture of oxides, because the amount of separation into basic and acid chlorides by each operation must depend very much upon the temperature of the muffle and the length of time during which the heat is applied. In the second place, it must be noted that, while a very nearly pure yttria is obtained in three operations, this does not represent the whole quantity of the earth in the compound. It will also be seen that a decided advantage must be secured by making mixtures of the products having nearly the same atomic masses, and then applying the method of separation to these.

Other applications of the method give, as I will now show, substantially similar results: The next substance examined was a mixture of oxides received from Dr. Shapleigh, and obtained from residual mother-liquors of cerite and monazite salts. The oxide was dissolved in chlorhydric acid, and purified by a current of sulphydric acid. Of the mixed oxalates,—

(69) 0.5622 gram gave 0.1715 gram $C_2O_3 = 30.50$ per cent.
(70) 0.4782 gram gave 0.1458 gram $C_2O_3 = 30.50$
(71) 0.4355 gram gave 0.1326 gram $C_2O_3 = 30.47$
(72) 0.6100 gram gave 0.2778 gram $R_2O_3 = 45.55$
(73) 0.6904 gram gave 0.3141 gram $R_2O_3 = 45.50$
      Atomic mass 137.25.

I also determined the mean atomic mass after separating the cerite earths by means of sodic sulphate in the usual manner. Of course some yttria went down with the double sulphates.

(74) 0.2440 gram gave 0.0946 gram $C_2O_3 = 38.77$ per cent.

(75) 0.2438 gram gave 0.0946 gram $C_2O_3 = 38.80$

(76) 0.4597 gram gave 0.2146 gram $R_2O_3 = 46.68$

(77) 0.3570 gram gave 0.1668 gram $R_2O_3 = 46.72$

Atomic mass 106.05.

The oxides with atomic mass 106.05 were then treated by the oxychloride process.

Portion B_1 Left.

(78) 0.4027 gram gave 0.1505 gram $C_2O_3 = 37.38$ per cent.

(79) 0.5204 gram gave 0.1943 gram $C_2O_3 = 37.35$

(80) 0.6947 gram gave 0.3250 gram $R_2O_3 = 46.78$

(81) 0.9233 gram gave 0.4323 gram $R_2O_3 = 46.82$

Atomic mass 111.3.

Portion B_2 Left.

(82) 0.4127 gram gave 0.1464 gram $C_2O_3 = 35.49$ per cent.

(83) 0.3215 gram gave 0.1142 gram $C_2O_3 = 35.51$

(84) 0.5885 gram gave 0.2668 gram $R_2O_3 = 45.33$

(85) 0.6205 gram gave 0.2814 gram $R_2O_3 = 45.35$

Atomic mass 113.95.

Portion A_1 Right.

(86) 0.4332 gram gave 0.1630 gram $C_2O_3 = 37.63$ per cent.

(87) 0.3239 gram gave 0.1217 gram $C_2O_3 = 37.57$

(88) 0.6813 gram gave 0.3062 gram $R_2O_3 = 44.94$

(89) 0.6749 gram gave 0.3035 gram $R_2O_3 = 44.95$

Atomic mass 105.1.

Portion A_2 Right.

(90) 0.3317 gram gave 0.1161 gram $C_2O_3 = 35.02$ per cent.

(91) 0.3216 gram gave 0.1126 gram $C_2O_3 = 35.00$

(92) 0.6800 gram gave 0.2823 gram $R_2O_3 = 41.52$

(93) 0.6529 gram gave 0.2709 gram $R_2O_3 = 41.50$

Atomic mass 104.05.

B_2 Right.

(94) 0.3785 gram gave 0.1314 gram $C_2O_3 = 34.73$ per cent.

(95) 0.2882 gram gave 0.0999 gram $C_2O_3 = 34.68$

(96) 0.6187 gram gave 0.2676 gram $R_2O_3 = 43.25$

(97) 0.6421 gram gave 0.2770 gram $R_2O_3 = 43.24$

Atomic mass 110.45.

A₂ Left.

(98) 0.3458 gram gave 0.1290 gram $C_2O_3 = 37.31$ per cent.
(99) 0.4089 gram gave 0.1523 gram $C_2O_3 = 37.24$
(100) 0.6892 gram gave 0.3062 gram $R_2O_3 = 44.43$
(101) 0.5986 gram gave 0.2660 gram $R_2O_3 = 44.44$
    Atomic mass 104.75.

A₃ Right.

(102) 0.3002 gram gave 0.1162 gram $C_2O_3 = 38.73$ per cent.
(103) 0.3251 gram gave 0.1260 gram $C_2O_3 = 38.77$
(104) 0.6667 gram gave 0.3031 gram $R_2O_3 = 45.44$
(105) 0.7642 gram gave 0.3478 gram $R_2O_3 = 45.51$
    Atomic mass 102.75.

(106) B₃ Right.

(107) 0.3426 gram gave 0.1307 gram $C_2O_3 = 38.16$ per cent.
(108) 0.3401 gram gave 0.1298 gram $C_2O_3 = 38.18$
(109) 0.8197 gram gave 0.3728 gram $R_2O_3 = 45.46$
(110) 0.7623 gram gave 0.3467 gram $R_2O_3 = 45.47$
    Atomic mass 104.65.

These determinations exhausted the material employed. The following diagram brings together all the results.
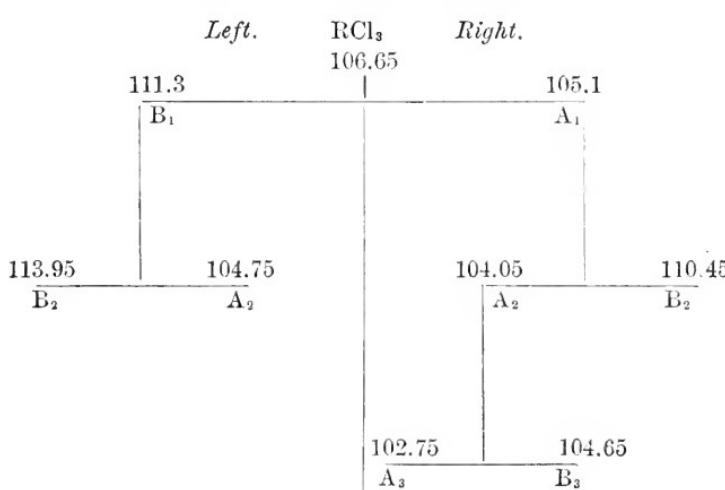
The diagram in the case of the oxides from cerite and monazite shows very clearly that, as with the oxides from gadolinite, the atomic masses B₁, B₂, B₃ increase, while those of A₁, A₂, A₃ diminish, but at a different rate, perhaps, as already remarked,

because the conditions were not precisely the same. It seems very desirable that similar experiments should be made with the basic-nitrate process, which has been so much used, so as to determine which method gives results that converge most rapidly toward the atomic masses of pure oxides. Only in this manner can the relative values of the two methods be determined. I consider it probable that further experience with the oxychloride process will lead to a very material shortening of the process. I have employed for the most part porcelain crucibles holding about 130 cc., but with larger muffles it would be easy to work up a kilogram of oxides at each operation. Also much is to be expected from a judicious mixture of the different products on the right and left having nearly the same atomic masses. All points fairly considered, I am I believe justified in offering the oxychloride process as worthy of further trial.

It appeared possible that basic bromides might be more advantageous than basic chlorides as means of differentiation, but experiments made were not conclusive on this point. Observing the formation of beautiful, well defined crystals when the oxides from gadolinite and the cerite and monazite residues were dissolved in chlorhydric or bromhydric acid, and the solutions evaporated to a syrupy consistence, I examined two cases. The perfectly colorless and easily soluble crystals obtained from gadolinite earths free from cerite earths by chlorhydric acid after two successive crystallizations were analyzed.

(111) 0.3248 gram gave 0.1293 gram $C_2O_3 = 39.82$ per cent.
(112) 0.3000 gram gave 0.1450 gram $R_2O_3 = 48.34$

The atomic mass is 107.10, so that the crystalline chlorides contained the earths in the same proportion in which they were obtained from gadolinite after separation of the cerite earths.

Precisely the same result was obtained with crystallized bromides prepared by dissolving the crude oxides from the cerite and monazite residues in bromhydric acid and evaporating. The beautiful colorless crystals were not quite free from the mother-liquor. Of these crystals,

(113) 0.3418 gram gave 0.1064 gram $C_2O_3 = 31.11$ per cent.
(114) 0.4266 gram gave 0.1325 gram $C_2O_3 = 31.07$
(115) 0.6110 gram gave 0.2879 gram $R_2O_3 = 47.13$
(116) 0.6896 gram gave 0.3293 gram $R_2O_3 = 47.02$

The atomic mass is 139.55, which is nearly the same as that obtained from the oxides directly, 137.25.

The mother-liquor from the crystals was also analyzed.

(117) 0.3750 gram gave 0.1171 gram $C_2O_3 = 31.25$ per cent.
(118) 0.3237 gram gave 0.1015 gram $C_2O_3 = 31.37$
(119) 0.6752 gram gave 0.3180 gram $R_2O_3 = 47.10$
(120) 0.8150 gram gave 0.3837 gram $R_2O_3 = 47.08$

The atomic mass corresponding is 138.45. From the above it appears that little, if anything, is gained by crystallization of the chlorides and bromides, at least in the cases cited.

The fact that potassic and sodic sulphates which do not give precipitates of double sulphates in cold saturated solutions of certain earths often give crystalline precipitates on boiling, has doubtless been observed. I do not find, however, that such observations have been noted in published papers. The following analyses will serve to show that valuable results may sometimes at least be obtained by this process.

A quantity of oxides from Samarskite, sent me by Dr. Shapleigh, was dissolved in chlorhydric acid, and precipitated cold by an excess of potassic sulphate. After filtering off the double sulphates, sodic sulphate was added and the solution boiled. An abundant white crystalline salt was obtained. After washing with a little boiling water the double salt was dissolved in chlorhydric acid, and oxalic acid added after large dilution. The oxalates were converted into oxides and these redissolved in chlorhydric acid and again precipitated with oxalic acid. The oxalates were then analyzed.

(121) 0.2853 gram gave 0.1217 gram R_2O_3.
(122) 0.3889 gram gave 0.1660 gram R_2O_3.
(123) 0.5558 gram gave 0.2256 gram C_2O_3.

Atomic mass 89.55, which does not sensibly differ from the received atomic mass of yttrium. From this it appears that yttria was separated in quantity by one operation after the separation of the cerite oxides.

Application of the cobaltamines to the separation of the oxides. —Many experiments were made to determine whether the sulphates of organic alkaloids would form double salts with the sulphates of the rare earths which could be made available for separations. These did not lead to satisfactory results, though

double salts were formed in some cases. It then occurred to me that the sulphates and other salts of various cobaltamines, on account of their disposition to form highly crystalline compounds, might be employed with advantage. Following are the results of this investigation.

A solution of sulphate of luteocobalt precipitates completely from their cold solutions as neutral sulphates the four cerite earths now known, namely, the oxides of cerium, lanthanum, praseodymium, and neodymium. The double sulphates are beautifully crystalline, have an orange-red color, and are very slightly soluble in cold water, but, practically at least, insoluble in boiling water. They are soluble in acids, and sometimes crystallize from weak acid-solutions. All these compounds appear to have the same constitution, which is that of the salts discovered many years since by myself, and analyzed in my laboratory by C. H. Wing.[1] I find, however, that the constitution of both the luteo- and roseo-salts may be much more accurately represented by the formulas:

$$\text{I. } 2\{Co_2(NH_3)_{12}(SO_4)_3 + Ce_2(SO_4)_3\} + 3aq.$$
$$\text{II. } 2\{Co_2(NH_3)_{12}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 3aq.$$
$$\text{III. } 2\{Co_2(NH_3)_{10}(SO_4)_3 + Ce_2(SO_4)_3\} + 9aq.$$
$$\text{IV. } 2\{Co_2(NH_3)_{10}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 9aq.$$

Mr. W. J. Karslake has arrived independently at the same formulas, and has calculated the percentages as required by them.

For Formula I.

		Calculated.	Found.		
24NH₃	408	16.93	16.75 (loss)		
4Co	236	9.79	9.31		
4Ce	560	23.24	24.10		
12SO₄	1152	47.80	47.77		
3H₂O	54	2.24	2.07		
	2410	100.00			

For Formula II.

		Calculated.	Found.		
24NH₃	408	17.97	17.73 (loss)		
4Co	236	10.40	10.80	10.74	10.44
3Ce	420	18.57	16.90	17.27	17.54
12SO₄	1152	50.75	51.80	51.83	52.22
3H₂O	54	2.37	2.47	2.21	2.39
	2270	100.00			

[1] Am. J. Sci. [2] **49**, 363.

For Formula III.

		Calculated.	Found.
20NH_3	340	14.72	14.24 (loss)
4Co	236	10.22	10.39 9.60
3Ce	420	18.18	18.18 19.36
12SO_4	1152	49.86	49.73 49.97
9H_2O	162	7.02	7.00 7.31
	2310	100.00	

For Formula IV.

		Calculated.	Found.
20NH_3	340	13.88	15.13 (loss)
4Co	236	9.64	9.90
4Ce	560	22.85	20.99
12SO_4	1152	47.02	47.23
9H_2O	162	6.61	6.75
	2450	100.00	

The analyses are those of Wing. Recent determinations of the molecular masses of the cobaltamines have shown that the chlorides, for example, of roseocobalt and luteocobalt are represented respectively by the formulas $Co(NH_3)_5Cl_3$ and $Co(NH_3)_6Cl_3$. I have kept the old formulas only to permit an easy comparison with those given by Wing, and the matter is not one of consequence in this place. It may also be remarked that, as cerium is at present the only one of the group which forms a well defined oxide higher than R_2O_3, the two formulas II and IV cannot be generalized by substituting the symbols of other elements for that of cerium. I have endeavored, however, to prepare such compounds by adding a solution of $Ce_2(SO_4)_3$ to one containing the sulphates of oxides other than the cerite oxides, and then adding some oxidizing agent, as for instance potassic permanganate, chlorine, or bromine. No decisive results were obtained. It is at least probable that all the earths the sulphates of which in cold solutions give only slightly soluble double sulphates with potassic and sodic sulphates will also give insoluble double sulphates with sulphate of luteocobalt. These earths are, so far as now known, Ce_2O_3, La_2O_3, Nd_2O_3, Ps_2O_3, Sm_2O_3, Sc_2O_3, while the following give soluble double sulphates: Er_2O_3, Y_2O_3, Yb_2O_3, and Tb_2O_3. The four cerite oxides cited are not the only ones which give insoluble crystalline precipitates with sulphate of luteocobalt in the cold, but I am not at present able to give more accurate

information on this point. On the other hand, we meet in the case of luteocobalt sulphate with some of the relations which present themselves when the alkaline sulphates are employed. Thus sulphate of yttria is not precipitated by sulphate of luteocobalt when alone, but when mixed with the sulphates of the cerite group more or less of a double sulphate of luteocobalt and yttria is always thrown down, and the same appears to be true for the sulphates of some other earths. In such cases the mixed sulphates of earths and luteocobalt should be gently heated in a muffle until the cobaltamine is completely decomposed and the excess of sulphuric acid is expelled. The residual sulphates of cobalt and the earths should then be dissolved in cold water, filtered, and again precipitated by sulphate of luteocobalt, allowing the mixture to stand twenty-four hours. The supernatant liquid appears then to contain all but the four cerite earths. This point is, however, not yet sufficiently proved, and I reserve it for further investigation.

The solution from which the double sulphates of the cerite earths and luteocobalt have been separated by decantation or filtration usually gives a more or less abundant crystalline precipitate on boiling. The filtrate from this again gives a precipitate with ammonia. The above stated facts are precisely those which we meet with in employing the alkaline sulphates in place of the sulphate of luteocobalt. I have also employed the sulphato-chloride of luteocobalt, $Lc_2(SO_4)_2Cl_2$, as a precipitant, and find that double salts are sometimes formed which are much more insoluble than those obtained with the sulphate, excepting only in the cases of the four cerite earths. These contain chlorine as well as sulphuric oxide, and they are sometimes at least formed when sulphate of luteocobalt is added to a solution containing the chlorides of metals of the cerium and yttrium groups. Sulphate of roseocobalt gives in general the same result as sulphate of luteocobalt, only the salts formed in this case are more soluble in both cold and hot water. Experiments with the sulphates of xanthocobalt and croceocobalt have not yet led to valuable results. Certain sulphates of the earths appear to give with sulphate of luteocobalt only hydroxides of the metals, $R(OH)_3$. In this case it seems more probable that a true double sulphate is at first formed and then decomposed, sulphuric acid being set free.

The following results may be of interest in this connection. A portion of earths from Fergusonite sent me by Dr. Shapleigh was converted into sulphates; the cerite earths had been separated by sodic sulphate, and the solution of the earths gave no further precipitate with this. A solution of sulphate of luteocobalt gave no precipitate with this solution in the cold, but on boiling a very abundant crystalline precipitate, insoluble or very slightly soluble in boiling water. The filtrate from these crystals gave only a small precipitate with ammonia, so that the luteocobalt salt must have contained almost all the earths other than the cerite earths. These are known to consist chiefly of yttria. The crystalline precipitate obtained as above by boiling, and insoluble in boiling water, dissolved completely in a large quantity of cold water. The nitrates of roseocobalt and luteocobalt give, in many cases at least, finely crystalline precipitates with the nitrates of the earths. In certain cases, white gelatinous precipitates of hydroxides are formed at the same time, probably as in the case of the sulphates above cited, in consequence of the formation of double nitrates and their subsequent decomposition into free acid and hydroxide. .This makes a new mode of differentiation which may prove to be of use, and to which I shall return hereafter. As an instance I may cite the case of the neutral nitrates of the gadolinite earths, from which the cerite earths have been separated by sodic sulphate. A strong solution of these nitrates gives with nitrate of roseocobalt, $Rc(NO_3)_3$, in a short time a bright orange, highly crystalline, and a dirty white, gelatinous precipitate. Both contain earths. The same is true for neutral nitrates from Samarskite, and from the cerite and monazite residues already mentioned. The nitrate of roseocobalt must be in excess. I have already stated that the action of the sulphates of roseocobalt and luteocobalt upon the sulphates of the earths closely resembles that of the alkaline sulphates. The advantage of using the cobaltamines consists, in part, in the fact that the double sulphates of these and the earths are highly crystalline and exceptionally well defined, and that they are in some cases at least very much less soluble than the alkaline double sulphates. The chief disadvantage is that the cobaltamines must be specially prepared for use, and that the most valuable of them—the sulphate of luteocobalt—is not easy to prepare in quantity and in a state of purity. Professor Morris Loeb has, however, found that sulphate of roseocobalt may be converted

into sulphate of luteocobalt by heating with strong ammonia water under pressure, as for instance in sealed tubes; and as the sulphate of roseocobalt is easily prepared, this process is perhaps the best.

A solution of sulphate of luteocobalt gives a very insoluble yellow crystalline precipitate with sulphate of thoria, $Th(SO_4)_2$. It gives also slightly soluble precipitates with uranic sulphate, UO_2SO_4, and with a solution of ferric alum which has undergone dissociation by solution. This last precipitate appears to have the formula $Fe_2O.(SO_4)_2 + Lc_2(SO_4)_3$.

It is my hope to be able to return to the subject in greater detail.

Relations of the oxides to lactic acid.—A portion of the oxides obtained from Samarskite by Dr. Shapleigh after the cerite oxides had been separated by sodic sulphate was boiled with pure lactic acid, and gave an amethyst-red solution. On standing, this solution gave two kinds of crystals, which were very distinct and well defined. These were beautiful red flat prisms, and distinct bright yellow granular crystals. The quantity was too small to permit a more thorough examination, and I did not obtain the same result a second time with other Samarskite oxides. In one experiment, however, the solution of the oxides was deep orange, and after a time deposited crystals with a fine orange color.

The lactates of the cerite earths and of the Samarskite earths which have not been treated with potassic or sodic sulphate give beautiful white feathery crystals, which dissolve with difficulty in hot water.

Relations of mercurous nitrate and mercuric oxide to cerite earths.—A solution of mercurous nitrate gives in general no precipitate with neutral nitrates of the cerite earths. In one experiment, however, in which I employed nitrates from a commercial oxalate, added a solution of mercurous nitrate, and then boiled with free mercuric oxide, the color of the oxide changed to a grayish tint. After filtering and washing, the filtrate was found to contain abundance of didymium (Nd and Ps). The precipitate after washing with boiling water was heated to redness in a platinum crucible, when a clear yellow powder remained. This dissolved in dilute nitric acid to a colorless liquid, which gave no didymium bands with the spectroscope. On adding water to the nitric acid solution a beautiful bright yellow crystalline powder was

thrown down. When the oxides were treated with sulphuric acid a white crystalline mass was formed. Hot water gave with this a fine bright yellow crystalline precipitate. I did not obtain these results with any other samples of cerite oxalates. So far as I am aware no known earths exhibit the reactions with nitric and sulphuric acids above described.

Relations of the Samarskite oxides to acid molybdates, and to phospho-tungstates and phospho-molybdates. — To determine whether any of the oxides contained in Samarskite were capable of forming complex inorganic acids the following experiments were made with a bright yellow mixture of oxides prepared by Lawrence Smith's process with fluohydric acid. The quantity at my disposal was less than five grams, and I am not certain that the cerite oxides had been removed by sodic sulphate.

1. With 10 : 5 phospho-molybdate of ammonium. The mixed oxides dissolved very easily on boiling with solutions of the phospho-molybdate, giving a fine orange solution. The action of the solution of phospho-molybdate upon the oxides seemed to give instantly a crystalline mass, which on boiling with some excess of phospho-molybdate dissolved. The solution gave beautiful orange-brown crystals, but after twenty-four hours the solution was clear and had a fine rose-color. This solution gave no absorption bands with the spectroscope. With ammonic oxalate it gave a white crystalline precipitate with a clear rose-red solution. This on evaporation to dryness in a platinum vessel gave a rose-red mass, which when heated fused to a greenish mass. The white oxalate settled slowly. The orange crystalline salt dissolved almost completely in boiling water, but some yellow crystalline matter remained. On standing, the solution deposited crystals of a yellow salt.

2. With 14 : 6 molybdate of ammonium. A solution of 14 : 6 molybdate of ammonium (commonly written $7MoO_3.3(NH_4)_2O$) also readily dissolved the mixed oxides and gave a deep orange solution. On standing twenty-four hours this gave bright yellow and afterwards very beautiful glittering orange-red crystals. The two kinds of crystals redissolved gave with mercurous nitrate a pale yellow flocky precipitate, which on boiling and standing became bright yellow and highly crystalline. The least soluble crystals were also redissolved separately, and after twenty-four hours crystallized in beautiful prehnitic groups. The orange

mother-liquor from these crystals gave the reaction with mercurous nitrate mentioned above. It seems probable from the above that 14 : 6 molybdate of ammonium gives at least two distinct salts.

3. With 24 : 2 sodic phospho-tungstate. A solution of this salt also dissolved the Samarskite oxides very readily on boiling, giving a fine orange-red solution which soon deposited an abundance of yellow needles. These dissolved readily in hot water to a yellow solution with an orange tint. Yellow needles quickly formed in abundance. After an hour the still slightly warm mother-liquor was poured off and allowed to stand. Two kinds of crystals separated,—very distinct, rather large granular orange crystals in much the larger quantity, and very small granular yellow crystals, differing much from the last in appearance. The two kinds of crystals were dissolved together in hot water, and after a time gave flocky masses of yellow crystals.

I did not succeed in obtaining the same results with other preparations of Samarskite oxides. This will not surprise those who have worked with the rare earths, and who have noticed the difference in the reactions which depends upon difference in the proportions of the mixed oxides. It has, I believe, escaped notice that the same occurs with mixtures of the different metals of the platinum group, as long since shown by Claus.

The compounds with molybdic oxide and with phospho-molybdic and phospho-tungstic acids may prove to be only salts of the earths, and not of complex acids. They appear to deserve further attention as means of separation. As the minerals belonging to the same group with gadolinite resemble each other very closely in their physical characters, it is possible that the yellow oxides above mentioned were not prepared from Samarskite, but from some other mineral.

Analyses 1 to 46 and from 69 to 122 inclusive were made by Mr. Edward L. Smith; from 47 to 68 inclusive by Mr. Wm. J. Karslake. My grateful acknowledgments are due to both.

ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.[1]

By Theodore William Richards and Elliot Folger Rogers.

In the course of an investigation upon the atomic weight of copper, recently conducted in this Laboratory, it was noted that cupric oxide prepared by the ignition of the nitrate always contains a considerable amount of occluded gas, which is composed mainly of nitrogen.[2] Cupric oxide prepared from the carbonate, on the other hand, appears to possess no such property of occluding gases. Since the material used by Hampe and others had all been made by the former method, it was at once evident that the occluded gas contained in the oxide was wholly responsible for the formerly accepted erroneous results for the atomic weight of copper.

The results of these experiments suggested the possibility that gases might be occluded by all oxides prepared in this way from the nitrates. It became a matter of much importance to test the point, for such oxides have often furnished the starting-point for determinations of atomic weights.

The method adopted in the present research was precisely similar to that used in the case of the cupric oxide. Since it is by no means certain that indefinite heating in a vacuum could drive out all the gas from the compact, often crystalline, compound under examination, the material was dissolved in acids under such conditions that the gas set free could be measured and analyzed.

The simple apparatus needed has been described and explained in the paper already quoted. The material to be investigated was placed in the largest bulb of the bulb-tube shown in the accompanying diagram, and the tube was about half-filled with cold water which had been thoroughly boiled. The whole was then connected with the water-pump, and freed from adhering air bubbles by agitation in the partial vacuum,—the water being allowed to boil gently under the reduced pressure. Subsequently,

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[1] Read before the American Academy of Arts and Sciences, May 10, 1893, and reprinted from the Proceedings of that Academy.

[2] Theodore W. Richards: Proc. Am. Acad. Sci. **26**, 281. In 1868 Frankland and Armstrong pointed out this fact; but their statement lacked definiteness, and has since been largely forgotten.

the tube was filled with boiled water and returned to its normal
horizontal position.   Pure acid was now run in from a pipette, a
short piece of glass rod within the large bulb furnishing a means
of agitating the oxide during its solution.   The gas which was set
free was finally collected and measured in the sealed end of the
apparatus. In the concluding experiments, where greater accuracy
was desired, the gas was transferred, and remeasured in a tube
which had been carefully calibrated by means of mercury.
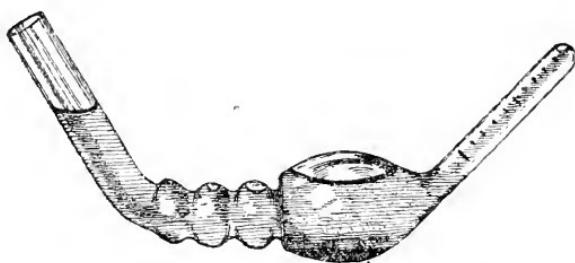
The gas was analyzed with the help of a small Hempel's appa-
ratus made for the purpose.   The burette with which the first ten
analyses were made was about 7 mm. in internal diameter and
could be read to a fiftieth of a cubic centimeter, while that used
for the later analyses was only 4 mm. in diameter and could be
read with reasonable certainty to the hundredth.   The portion of
the gas absorbed by caustic potash was assumed to be carbon
dioxide, and the further portion which was absorbed by alkaline
pyrogallol was assumed in like manner to be oxygen. The residue
was perfectly inert, and was undoubtedly nitrogen.   One sample
of this residue obtained from zincic oxide was mixed with oxygen
and subjected to the spark of an induction-coil, without diminution
in volume.   The apparatus and chemicals were tested from time
to time by analyses of air.

In every case, the gas while saturated with aqueous vapor was
measured at the ordinary temperature and atmospheric pressure
of the room.   The variations from the mean values of 22° and
76.0 cm. were not sufficient to need attention in crude work of this
kind, when working upon such very small quantities of gas.

Zinc Oxide.

Preliminary experiments with this substance gave results exactly
corresponding to those obtained from cupric oxide.   If the sub-

stance was prepared by ignition of the nitrate, very considerable amounts of gas were found to be occluded; while material of a similar grade of purity in every other respect, made by heating zincic carbonate, appeared to contain no trace of gas.

The oxide used in the first three experiments was made by treating so-called pure zinc with nitric acid, evaporating to dryness, redissolving the zincic nitrate in water with the addition of a little nitric acid, precipitating a small amount of iron with ammonia in slight excess, evaporating the filtrate, and igniting the residue. This gave a faintly yellow oxide.

For the second series, a nearly neutral solution of fairly pure zincic chloride was precipitated while boiling by a solution of sodic carbonate. Part of the basic carbonate thus formed was ignited directly, the oxide thus produced containing no occluded gas (Experiment 4). The remainder was dissolved in nitric acid, evaporated to dryness, and ignited to the full heat of the blast-lamp in a porcelain crucible. Experiments 5, 6, and 7 are analyses of this yellowish sample.

For the third series a solution of " chemically pure " zincic nitrate was allowed to stand over an excess of zinc for some time. The filtered solution was evaporated until a portion of the nitrate had been converted into the basic salt. The whole was then poured into distilled water, and a solution of normal nitrate was thus obtained after the basic salt had been filtered off. This solution was treated a number of times with zincic hydrate,—which had been precipitated by ammonia and washed until free from the salts of this base,—and allowed to stand. The filtered solution was evaporated to dryness and heated in a porcelain crucible to about 240° C. over a ring burner. Part of this was analyzed at once (Experiment 8), part heated by a Bunsen burner (Experiments 9 and 10), and part ignited at a very high temperature in a Hempel clay furnace with the blast-lamp and bellows (Experiments 11 and 12). Experiment 13 was made with a soft white oxide prepared from the basic nitrate.

Analyses 14 to 27 inclusive were made from oxide obtained as follows: Pure white zincic oxide of commerce was dissolved in nitric acid, and carefully washed zincic carbonate was added to this solution in slight excess. The whole was allowed to stand with occasional shaking for some time, and finally filtered and evaporated rapidly by boiling. This gave a sample of the oxide

which was very nearly white after intense heating in a double porcelain crucible.

In Experiments 22 and 23, pure oxygen was introduced into the flame of the blast-lamp used for igniting the zincic oxide, the bottom of the outer crucible being melted where the flame struck it. The material analyzed in Experiment 22 was taken from the layer nearest to the zincic silicate formed in the bottom of the crucible by fusion of the glaze, and that used in Experiment 23 was taken from the top. The zincic oxide of Experiment 24 was heated to a bright yellow heat in the same way. All the edges of the porcelain were rounded, and the cover and the crucible itself were fused to the heavy iron supports on which they rested. After twelve minutes the iron itself began to burn and the ignition was stopped. The oxide was found to be "sintered together," and was of a grayish color, as if it had been reduced in part. The inference was corroborated by the presence of zincic oxide on the cover of the crucible and on the sides of the stack of the furnace. The zincic oxide used in Experiment 25 was treated in a similar manner, but proved to be still darker in color. It was afterwards ignited for some time in an atmosphere of oxygen, in order that no reduced metal might be left.

The materials used in Experiments 26 and 27 were separate samples heated in a double crucible, with the cover of the inner crucible fitting inside the outer one, instead of covering both. This arrangement rendered less likely the entrance of reducing gases, and allowed freer play of air in the furnace. After the latter had been thoroughly heated by the ordinary blast-lamp, oxygen was slowly turned on through a Y tube, to replace a large part of the air in the flame. This gave an intense white heat, which melted and burned the tip of a file in the fraction of a minute. In Experiment 27 the glaze of the inner crucible was fused, and the platinum which separated the two crucibles was cemented to the outer crucible. The crystalline residue of zincic oxide after this treatment was white with the faintest trace of yellow, but no sign of gray. As the crucible would not stand a higher heat, and as any quantitative determination could scarcely be carried on at a higher temperature, no attempt was made to push the heat further.

The fifth series of determinations was made with the object of discovering whether the trace of silica and alkali dissolved from the glass and porcelain might be responsible for the occlusion of

the gases. First, a sample of the purest zinc that could be obtained was treated with a small amount of pure nitric acid in a porcelain dish, and the solution evaporated to small bulk in the presence of an excess of zinc. Upon dilution the basic nitrate, which contained most of the impurities not deposited upon the zinc, was precipitated and removed by filtration. The solution was then evaporated to dryness and the residue ignited in porcelain. (See Experiments 28 and 29.) Another sample of zinc was dissolved in a similar way in platinum, and the resulting solution of the pure nitrate was divided into several portions. One portion was evaporated in glass and ignited in porcelain, the residue containing somewhat more gas than that which had been treated wholly in porcelain. (See Experiments 30, 31, 32, and 33.) Another part was evaporated and ignited in platinum (Experiment 34). This sample was undoubtedly reduced in part by the diffusion of gases from the flame.[1] Still another portion was ignited for a short time only in platinum, the ignition being completed in porcelain (Experiment 35). A fourth portion was ignited for a short time in an open platinum dish with free access of air (Experiment 36). Finally, the remainder of the solution of pure zincic nitrate was evaporated and ignited in a platinum vessel enclosed within one of porcelain. This specimen was not exposed to the action of reducing gases, and upon solution it evolved almost exactly the same amount of gas as the specimen which had been prepared in glass and ignited in porcelain. (See Experiments 37 and 38.)

Experiment 39, using zincic oxide prepared from the carbonate, was made to test again the accuracy of the method.

The weight of zincic oxide taken for each individual experiment is tabulated in the second column of the following table, and the third column indicates approximately the conditions used for the ignition of the different portions. The volume of gas given off on the subsequent solution of the zincic oxide in sulphuric acid is recorded in the fourth column, while the fifth contains the same data reduced to the standard of ten grams of zincic oxide. The sixth column contains a record of the analyses of the gases, and the seventh supplies information upon a few minor points connected with individual results.

[1] Erdmann: Ann. der Phys. Pogg. 62, 611; Morse and Burton: This Journal 10, 311-321.

No. of Exp.	Weight of Zincic Oxide.	Time and Temperature of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of ZnO.	Analysis of Gas by Volume.	Remarks.
	grams.		cc.	cc.		
1	1.375	Blast-lamp.	1.6	12.0		
2	1.19	"	1.45	12.2		
3	1.225	"	1.53	12.5		
4	1.1	"	0.00	00.0		From carbonate.
5	1.05	"	2.1	20.	$CO_2 = 2.0\%$	
6	1.08	"	2.1	19.4	$O_2 = 55.5$	
7	1.075	"	2.15	20.	$N_2 = 42.5$	
8	1.27	240° C.	0.00	00.0		Gave test for nitrates.
9	1.005	Bunsen flame.	.70	7.0		
10	1.065	"	.78	7.3		
11	1.22	Blast-lamp Hempel furnace.	.58	4.7		
12	1.91	"	.92	4.8		
13	1.05	Water-blast Hempel furnace.	.20	1.9		Made from basic nitrate.
14	1.07	Water-blast furnace 30 min.	.75	7.0		Fourth series.
15	1.00	"	.71	7.1		
16	1.02	Blast.	1.52	14.9	$CO_2 = 1.3\%$ $O_2 = 53.8$ $N_2 = 44.8$	
17	1.10	Water-blast Furnace 2 hr.	.35	3.2	$O_2 = 9.1$ $N_2 = 90.9$	Partly reduced.
18	1.20	" 3½ "	1.12	9.1		18–21 heated in double crucible by water-blast in furnace. Samples removed from time to time.
19	1.06	" 5 "	.83	7.8		
20	.85	" 6 "	.46	5.4		
21	.92	" 6½ "	.53	5.8		
22	1.07	Furnace 6½ hr. Oxygen flame, 15 min.	.42	3.9	$CO_2 = 0.0\%$ $O_2 = 16.9$ $N_2 = 83.1$	Layer next the silicate.
23	1.125	The same.	.48	4.3		Upper layer.

No. of Exp.	Weight of Zincic Oxide.	Time and Temperature of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of ZnO.	Analysis of Gas by Volume.	Remarks.
	grams.		cc.	cc.		Partially reduced and reoxidized.
24	1.03	Oxy. fl. 15 min.	.24	2.3	$O_2 = 16.7\%$ $N_2 = 83.3$	
25	1.105	" 30 "	.19	1.7		Reduced more than Ex. 24 and reoxidized.
26	.72	White heat 20 min.	.33	4.6	$CO_2 = 0$ $O_2 = 24\%$ $N_2 = 76$	White after ignition.
27	1.0125	White heat 35 min.	.45	4.4		" "
28	1.05	Water-blast ½ hr.	.42	4.0		Fifth Series.
29	1.019	1½ hr.	.37	3.6		
30	1.34	Bunsen Flame 30 min.	.28	2.10		Probably contained nitric acid.
31	1.05	Water-blast 30 min.	.97	9.2		
32	1.0035	Water-blast 1 hr.	.68	6.8		
33	.9765	1½ hr.	.63	6.4		
34	1.03	Water-blast ½ hr.	.175	1.7		Partially reduced.
35	1.08	½ hr.	.35	3.2		Less reduced.
36	1.50	20 min.	.82	5.46		Possibly reduced in part.
37	1.004	1½ hr.	.68	6.8		
38	1.018	2 hr.	.68	6.7		
39	1.00		0.00	0.00		Prepared from carbonate.

It is evident that we are dealing here with a phenomenon similar both qualitatively and quantitatively to that observed in the case of copper. Zincic oxide prepared from the nitrate occludes a very appreciable quantity of nitrogen and a somewhat variable quantity of oxygen. Continued application of heat tends to drive out both gases, the oxygen being less firmly held than the nitrogen; but the highest heat which we were able to obtain was insufficient

wholly to eliminate either gas. Under like conditions, specimens of zincic oxide made from zincic nitrate which had been obtained in a number of different ways appeared to hold approximately the same amounts of gas. It is almost, if not quite, impossible to prepare the oxide in this manner in a state wholly free from solid impurities taken from the containing vessel during the ignition of the purest possible zincic nitrate. The effort was made in the preceding series of analyses to prepare samples which must contain wholly different kinds of impurities. The fact that these different samples contained almost equal amounts of gas shows with reasonable certainty that the impurities are not responsible for the occlusion.

It is noticeable that the oxide obtained at a very low temperature, which still contained traces of zincic nitrate, contained little or no occluded gas (Experiments 8 and 30); also that six specimens which had been suspected of partial reduction contained much less gas than similar material free from this suspicion (Experiments 17, 24, 25, 34, 35, and 36).

NICKELOUS OXIDE.

The series of experiments with nickelous oxide led to results not unlike those with zincic oxide. In this case sulphuric acid proved unsatisfactory as a solvent, and hydrochloric acid was adopted. A solution containing about 20 per cent. of hydrochloric acid gas was freed from air by continued boiling, rapidly cooled, and run into the tube containing the oxide of nickel. On account of the very slow action of the cold acid the tube was warmed after exhausting the air as usual. The gas set free was measured as before.

In order to prove the accuracy of the method a gram of zincic oxide prepared from the carbonate was dissolved in hot hydrochloric acid in precisely a similar way. No trace of gas was evolved during this solution.

It was thought unnecessary to make a series of experiments as elaborate as that made with the zincic oxide. Nickelous nitrate was evaporated to dryness in porcelain and ignited fifteen minutes in a blast-lamp and then a number of hours over a Bunsen burner in the furnace. (Analysis 1, below.)

A part of the nickelous oxide remaining was further ignited for two hours in the furnace by means of the water-blast. This was

used for the second analysis. A portion of the latter was ignited again in the furnace at the highest temperature we could obtain, by the addition of oxygen to the flame for about fifteen minutes, until the bottom of the outer crucible as well as the platinum foil between the two crucibles was melted away. The arrangement of data in the table is similar to that already described.

No. of Exp.	Weight of Oxide.	Vol. of Gas evolved.	Vol. of Gas calc. for 10 gr. NiO.	Analysis of Gas by Volume.	
1	1.14 grams	.469 cc.	4.11 cc.	$O_2 = 12.25$ per cent.	$N_2 = 87.75$
2	.997	.34	3.41		
3	1.13	.35	3.09	$O_2 = 8.8$	$N_2 = 91.2$

Magnesic Oxide.

The experiments with the oxide of magnesium led to very unexpected results, the amount of gas evolved upon the solution of this compound being five to twenty times as much as was obtained from zincic oxide, and over twenty-five times as much as from the oxide of nickel. More difficulty was found in decomposing the nitrate than before, and the remaining oxide was in a much harder and more compact state, and consequently more difficult to pulverize. The process used was similar to that employed in the case of the other oxides.

Magnesic nitrate made from pure nitric acid and magnesic carbonate of commerce was evaporated to dryness in porcelain. The residue was pulverized in an agate mortar, heated by means of the blast-lamp in a covered porcelain crucible, and cooled over calcic chloride. For a parallel experiment, a portion of the original carbonate was converted into the oxide by simple ignition, the magnesia formed in this way evolving only an extremely small amount of gas upon solution (Experiment 2 below).

A third portion of magnesic nitrate was made from pure magnesium ribbon and pure nitric acid, and the oxide was obtained from this salt by evaporation and ignition in porcelain as usual (Experiment 7).

Sulphuric acid was used for the solution of the magnesic oxide, as in the case of zincic and cupric oxides. The following table explains itself.

No. of Exp.	Weight of Oxide used.	Temperature and Time of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of MgO.	Analysis of Gas.	Remarks.
1	grams. .50	Blast-lamp, 30 min.	cc. 5.45	cc. 109.	$\{\begin{array}{l} O_2 = 66.6\% \\ N_2 = 33.4 \end{array}$	
2	about 1.0	" 1 hr.	.05	.5		Made from carbonate.
3	.50	" 1¼ hr.	5.86	117.2	$\{\begin{array}{l} CO_2 = 5.98 \\ O_2 = 53.7 \\ N_2 = 40.29 \end{array}$	Analyses made from one sample of oxide heated under different conditions. 1, 3, and 4 gave tests for nitrates with ferrous sulphate ; 5 and 6 did not.
4	.25	" 2¼ hr.	2.31	92.4	$\{\begin{array}{l} O_2 = 47.6 \\ N_2 = 52.4 \end{array}$	
5	.25	" 3¼ hr.	2.31	92.4	$\{\begin{array}{l} CO_2 = 2.2 \\ O_2 = 38.9 \\ N_2 = 58.9 \end{array}$	
6	.25	Oxygen-blast. 20 min.	2.04	81.6	$\{\begin{array}{l} O_2 = 34.3 \\ N_2 = 64.2 \end{array}$	
7	.25	Water-blast, 1½ hr.	2.31	92.4	$CO_2 = 1.5$	

The amount of gas occluded by magnesic oxide is thus much greater than that occluded by the oxides of copper, zinc, and nickel. The quantities of carbon dioxide recorded in the table are undoubtedly far from accurate, since the gas was collected over water. It is interesting to note that the amount of nitrogen evolved by the oxide upon going into solution was slightly increased up to a certain point by the increasing time and heat of the ignition, while the amount of oxygen was rapidly diminished.

No. of Exp.	Volume of Nitrogen found in 1 gram of MgO.	No. of Exp.	Volume of Oxygen found in one gram of MgO.
1	3.6 cc. Gas.	1	7.2 cc. Gas.
3	4.72	3	6.3
4	4.84	4	4.4
5	5.44	5	3.6
6	5.24	6	2.8

THE OXIDES OF CADMIUM, MERCURY, LEAD AND BISMUTH.

These oxides, the only other suspected ones which could be easily analyzed by the method in hand, all yielded negative results. The oxide of cadmium was distinctly crystalline, and contained only the merest trace of gas. The oxides of mercury, lead and bismuth obtained by the ignition of the corresponding nitrates also appeared to contain no occluded gaseous impurity.

Unfortunately, the oxides of antimony, iron, and a number of other metals, are not sufficiently soluble in acids to test with ease their power of occlusion by this method. It seems probable that interesting results might be obtained from them; hence in the near future other methods will be tried here, with the hope of determining if these oxides also occlude gaseous impurity.

THEORETICAL CONSIDERATIONS.

From the fact observed with both copper and zinc, that oxides which still contain a trace of nitrates, as well as those made from the carbonate, retain no imprisoned gas, it is readily inferred that the decomposition of a trace of nitric acid is alone responsible for the impurity. It is natural that this last trace of nitric acid should be confined below the surface, whence the gases resulting from its ultimate decomposition would find it hard to escape. On this supposition it is not unnatural that zincic oxide which has been partly reduced, and hence somewhat disintegrated, should contain less occluded gas than that which has not been thus reduced. Moreover, since magnesic nitrate is harder to decompose than the other nitrates, and the oxide is more compact, we should expect to find more gas occluded in this case than in the others. All these inferences agree with the facts. The difference in the rate of expulsion of the oxygen and of the nitrogen is interesting, and less easy to explain.

The negative results observed with a number of metals lead one to conclude that the physical condition of the oxides in these cases was so porous that even the last traces of nitrogen were allowed to escape. Indeed, cupric and zincic oxide made from very finely divided basic nitrates, obtained from aqueous solution, contained much less gas than samples which were obtained in a more compact condition by the direct ignition of the normal nitrate. This fact shows how much depends upon physical conditions.

It must be borne in mind that the occlusion of gases noted in this paper is a very different phenomenon from the retention of undecomposed oxides of nitrogen alluded to by Marignac,[1] Morse and Burton, and others. Nitrogen present in the state of gas could of course give no test with sulphanilic acid and naphthyl-

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[1] " Il est probable que l'oxyde de zinc et la magnésie ne sont pas les seuls oxydes qui retiennent aussi énergiquement des composés nitreux, lorsqu'on les prépare par la calcination de leurs azotates." Ann. Chim. Phys. (6) 1, 311, foot-note.

amine, or any other test for oxidized nitrogen. It is evident that the phenomenon we are now studying, like the other just spoken of, may be a very serious cause of error in many of the published determinations of atomic weights; these would hence appear lower than their true value, because of the extra material which is calculated as oxygen.[1] Before any quantitative results obtained in this way can be accepted as authoritative, definite proof must be brought forward of the absence of this source of error. It is to be hoped that the able experimenters who have recently worked upon zinc, nickel, magnesium and similar metals have preserved typical specimens of their final products. If this is the case, nothing could be easier than to determine the amount of occluded gas, if any is present, and to apply the necessary correction.

As long ago as 1887 one of us was engaged, through the suggestion of Professor Cooke, upon an investigation of the atomic weight of zinc ·depending upon the analysis of zincic bromide. The work was discontinued because of the many publications upon this subject which appeared before it could be completed. Since the results recorded in this paper appear to indicate that the last word has not yet been said upon the subject, the investigation of zincic bromide and chloride is now being continued in this Laboratory.

THE EFFECT OF PLATINUM IN IRON SOLUTIONS.

By R. W. Mahon.

When the residue of an iron ore insoluble in acid is fused in platinum with sodium carbonate, a quantity of platinum is imparted to the subsequent solution of the fusion in water and hydrochloric acid. When the fusion is made with about 7 grams of sodium carbonate in a 25-cc. crucible with clean bright surface, fusing before the blast-lamp for a few minutes, the loss in weight

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[1] The following are the elements whose atomic weights have been determined by means of the oxide made through action of nitric acid: Hydrogen (cupric oxide), Magnesium, Aluminium, Vanadium, Manganese, Nickel, Cobalt, Copper, Zinc, Gallium, Selenium, Tin, Antimony, Tellurium. See Meyer and Seubert: Atomgewichte, pp. 17-42; also for Nickel, Krüss: Z. anorg. Chem. **2**, 235; for Zinc, Morse and Burton: This Journal **10**, 311-321; for Magnesium, Burton and Vorce: This Journal **12**, 219; Chem. News **62**, 267.

of the crucible for one fusion is about 0.0008 gram. The presence of this much platinum when estimating iron by titration with potassium bichromate, after reduction by stannous chloride, dilution and addition of mercuric chloride in excess, is troublesome. Stannous chloride added to the hot hydrochloric-acid solution of ferric and platinic chlorides first reduces the iron and then the platinum. The solution which becomes gradually colorless during reduction of the iron to the ferrous state, again takes on a yellow tinge, due to the trace of platinous chloride formed. This minute quantity of platinous chloride colors the solution on account of the formation of one of the two compounds of platinous and stannous chlorides described by Kane,[1] being the one containing the most tin. The addition of mercuric chloride after dilution gives a solution with a precipitate suspended in it, the whole sometimes having a tinge of color; instead of giving, as in absence of platinum, a colorless solution with pure white mercurous chloride in suspension. Platinum being present, the titration with bichromate causes first the disappearance of color and next the oxidation of ferrous chloride, until finally drops taken from the solution no longer give a blue color with potassium ferricyanide. After this point has been reached a recurrent bluing is sometimes met with, especially if the solution stand a moment and a drop then removed be tested. Sometimes this recurrence is rapid enough to amount to a continuous coloration.

The interference of platinum in this method for iron estimation is well known to many, although there is no published reference to it. I have therefore sought to study the reactions which take place, and to devise a method for overcoming the difficulty.

In his study of the chloroplatinites, Nilson[2] speaks of the impossibility of preparing ferric chloroplatinite, as ferric chloride and chloroplatinous acid form ferrous chloride and ferroplatinate and ferriplatinate. The part of this reaction which is of interest in the present connection is the reduction of the ferric chloride by platinous chloride. The solution, acid with hydrochloric acid, obtained in the course of analysis just before dilution, is clear, and, as has been stated, of a yellow tint in presence of platinum; it remains clear upon dilution. If less acid were present and the solution much more copiously diluted, the platinum-tin chloride would be decomposed and precipitated, as described by Kane,

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[1] Phil. Mag. [3] **41**, 399. [2] J. prakt. Chem. [2] **15**, 282.

yet, even for slight acidity and extreme dilution, this reaction can be seen only when the quantity of platinum occurring in an analysis is several times as great as is usual in analyses of this kind. When then, in the course of analysis, mercuric chloride is added to the diluted solution, in addition to the mercurous chloride formed, the platinum is precipitated. The color of the solution with the precipitate in suspension is due to the platinum precipitate, the solution if filtered at this point being colorless. The quantity of platinum present in an analysis is too small to impart much color to the whole mass of mercurous chloride precipitated.

If to a solution of platinic chloride, strongly acid with hydrochloric acid, stannous chloride be added and then mercuric chloride in excess, three cases are to be distinguished :

1. The stannous chloride is added only in sufficient quantity to convert the platinic to platinous chloride.—The addition of mercuric chloride produces no precipitate.

2. The stannous chloride is added in six times the amount just mentioned, or in some intermediate amount.—The solution takes on a deep red tint if an appreciable quantity of platinum is used. The addition of mercuric chloride changes the red to yellow, and the solution then deposits a black precipitate.

3. The stannous chloride is added in more than six times the first mentioned amount.—In an actual analysis, the quantity of platinum being so minute, the stannous chloride will have been thus added. By close observation and working rapidly, the following changes are seen to take place upon addition of mercuric chloride : The color of the solution changes from red to yellow ; mercurous chloride is precipitated. If this is filtered out the yellow filtrate deposits a black precipitate. These precipitates first come down of a dark brownish-red color and then turn black. This change of color from reddish-brown to black is best seen when using a minute quantity of platinum. The same precipitate,[1] evidently mercurous chloroplatinite, was obtained by Nilson on adding mercurous nitrate to potassium chloroplatinite. He describes it as amorphous, dark brown, and rapidly turning black in the mother-liquor. Mercurous chloroplatinite is easily soluble in ferric chloride, yielding ferrous chloride, platinic chloride and mercurous

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[1] In a modification of the stannous-chloride method which I have suggested (This Journal 15, 360) the end-reaction is incorrectly described. The first few drops of stannous chloride in excess over that needed to reduce the iron, acting upon the platinum-mercury indicator, precipitate mercurous chloroplatinite.

chloride; the platinic salt then acting upon the mercurous to form mercuric chloride, and the platinous chloride formed reducing a further quantity of ferric chloride.

The same changes take place in an iron-estimation. The stannous chloride will have been added in sufficient excess to reduce all the iron and platinum, and to cause the precipitation of mercurous chloride and mercurous chloroplatinite—the conditions described in 3. At the commencement of the titration the tinge of color disappears, because the first few drops of bichromate oxidize some of the iron to ferric chloride, which then acts upon the mercurous chloroplatinite, forming platinic chloride, and adding a minute quantity of mercurous chloride to that already present. The platinic chloride at the moment of its formation is again reduced by mercurous chloride. The titration proceeds, and the same cycle of operations is repeated, until finally all the iron is oxidized, and the mercurous chloride all dissolved as mercuric. Thus a small quantity of platinum may introduce a large error into the estimation.

Although troublesome, the presence of platinum is not fatal to accuracy. From many iron ores when reduced to an impalpable powder, hydrochloric acid of 1.20 specific gravity dissolves practically all of the iron, leaving an amount so small that it may be disregarded even in accurate estimations. This is of course not always the case, and when a fusion must be made, the simplest way of avoiding error is to add stannous chloride with care, and cease when the color due to ferric iron has disappeared, and before that due to platinous chloride has begun. Another way is first to precipitate the iron in the fused and dissolved residue by means of ammonia, filtering on a small filter, and, after thorough washing, redissolve in hydrochloric acid and hot water, receiving in the beaker of precipitation. Thus a solution is obtained entirely free from platinum.

The following are four determinations of iron in the same ore. In Nos. 3 and 4 the causes leading to error were purposely exaggerated, although no platinum was introduced except that derived from the crucible.

	In the solution.	Percentage of iron In the fusion.	Total.
1.	57.57	1.20	58.77
2.	57.57	1.20	58.77
3.	57.57	5.84	63.41
4.	57.67	4.83	62.50

The causes leading to error when the platinum has not been separated before titration are: 1. The presence of much platinum introduced by protracted fusion; 2. A large quantity of free hydrochloric acid; 3. The addition of a large excess of tin.

It is desirable that fusion should be thorough, in order that decomposition may be perfect, and that a considerable quantity of hydrochloric acid be present to obtain sharp reactions. A distinct excess of tin has the advantage of certainty of complete reduction, and at a lower temperature, thus giving a cold solution finally after dilution.

The preliminary separation of platinum as described above is much to be preferred to the other way of working.

ON THE ACTION OF SODIUM ON ACETONE.

By Paul C. Freer.

Some three years ago I published two preliminary notices[1] describing the reaction which takes place when sodium is brought in contact with acetone mixed with a large volume of absolute ether, and at a later date I prepared a more extended paper on the same subject.[2] Since that time I have been able, by means of improved apparatus, to obtain large quantities of the products of the reaction at one operation, and as a consequence have been able much more accurately to determine the real changes which take place. As a result of these further investigations it has been proven that the sodium acetone formerly described as a uniform body, in reality consists of that substance mixed with a number of others.

In order definitely to settle the fact that a molecule of acetone contains a hydrogen atom that is replaceable by one of sodium, it is necessary to prove, in the first place, that hydrogen is evolved when sodium is brought in contact with the liquid in question, and, in the second place, that acetone can once more be separated, by addition of dilute acids, from the compound formed by this

[1] This Journal 12, 355; J. prakt. Chem. [2] 42, 470.   [2] This Journal 13, 319.

means. A long time ago Löwig and Weidmann[1] studied the action of potassium on acetone, discovering that the reaction between the metal and pure acetone is of such violence that if great care is not exercised the liquid takes fire; yet this catastrophe could be averted by sufficient cooling. No permanent gas is, however, developed. Fittig,[2] at a later date, observed that sodium attacks acetone with considerable energy, producing a flaky-white precipitate, which soon becomes brown upon the surface, but made no observations in regard to a gas which may possibly be developed. This investigator studied the action of ethyl iodide on the products of the reaction; he distilled the mixture and discovered that only ethyl iodide and acetone passed over, whereas, upon heating the solid remainder, a thick oil that soon deposited crystals of pinakon, was produced. Subsequently Städeler[3] also observed that anhydrous acetone develops no gas when brought in contact with sodium. In my former papers on this subject I have shown that acetone, if diluted with an indifferent solvent, liberates hydrogen when acted on by sodium. In spite, then, of this previous work I have repeated the experiments in a most careful manner, and have come to the conclusion that although pure acetone when treated with sodium liberates no trace of gas, nevertheless, if it is mixed with absolute ether, ligroïn or xylene it evolves hydrogen in increasing proportion with increasing dilution; the quantity of gas produced by dissolving a constant quantity of sodium reaching a maximum at a ratio of 1 of acetone to 100 of solvent, this maximum being about 62 per cent. of the amount calculated by theory. It is actually true, therefore, that acetone, provided the proper preliminary precautions are taken, will liberate hydrogen when brought in contact with sodium; when, however, no diluent is present, all of the gas is immediately used up for purposes of reduction, and even under the most favorable circumstances a considerable portion thereof disappears. The compounds produced by this reaction naturally contain sodium isopropylate and sodium pinakonate, in addition to acetone sodium, and it is also possible, as will be shown below, that the sodium compounds of mesityl oxide and of phoron are also formed—at least it has been shown that all of these substances are liberated from the white, flocculent precipitate on the addition of dilute acids.

[1] J. prakt. Chem. **21**, 54; Ann. der Phys. Pogg. **17**, 309.   [2] Ann. Chem. (Liebig) **110**, 23.
[3] *Ibid.* **111**, 277.

In order to determine whether the sodium in acetone sodium is contained in a natroxyl group or is attached to carbon, I have studied the action both of benzoyl chloride and of ethyl chlorcarbonate on the mixture of sodium compounds, and, as will be seen from that portion of this paper which deals with the experimental work, the results obtained with the former reagent admit of the definite conclusion that the sodium in sodium acetone is in reality attached to oxygen, and that therefore the substance in question possesses the following formula: $CH_3 — CONa = CH_2$, so that it is to be regarded as the sodium compound of β-allyl alcohol.

Experimental Part.

Determination of the Relative Quantity of Hydrogen which is evolved when Sodium acts upon Acetone.

The acetone which was used for all of these and many of the following experiments was prepared from the sodium bisulphite compound. It was dehydrated by repeated distillation over fused calcium chloride, followed by shaking with an excess of phosphoric anhydride,[1] pouring off the liquid, fractioning, and finally twice distilling the liquid, which is presumably perfectly free from water, after the addition of about 0.5 gram of sodium before each operation. That portion which had a boiling-point of $56.5°–57.5°$ was used exclusively, and was always kept over fused sodium sulphate.[2]

It very soon became apparent that Löwig and Weidmann's, as well as Städeler's, statements were correct, namely, that pure acetone develops no hydrogen when brought in contact with the alkali metals, as the following experiment proves: 0.5 gram of pure sodium, finely powdered under toluene, was sealed in a small glass bulb also filled with that liquid, and the bulb was then placed in a tube containing pure acetone. The tube was then drawn out to a bent point 10 cm. in length, which was sealed after cooling the

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[1] This operation was twice repeated.

[2] When, at a later period in the research, it was discovered that some isopropyl alcohol is always formed when sodium is dissolved in acetone, it occurred to me that the criticism could be made that the evolution of hydrogen might be due to isopropyl alcohol which might be liberated when the acetone, previously treated with sodium, was distilled. Although this seemed extremely improbable, as in all likelihood the isopropyl alcohol would be present in the form of sodium isopropylate, I nevertheless repeated all of the work, using acetone which had been dehydrated by shaking four times with phosphoric anhydride, pouring off and distilling. There is no doubt that this substance is perfectly anhydrous, although the use of sodium was entirely avoided.

entire apparatus to 0°. The glass bulb was then broken by shaking and, after the completion of the reaction, the temperature was once more brought to 0°, and the tip of the enclosing tube was opened under water. The pressure was found to be unchanged, and hence no gas had been liberated. Entirely different results are observed, however, if the acetone has been diluted by means of some indifferent solvent before adding the metal.

FIG. 1.

In order accurately to determine the amount of gas which is liberated under differing experimental conditions of solution I finally constructed the following apparatus, which admirably answered my purpose : About 0.1 gram of sodium is cut and weighed under liquid paraffin and then placed in the bulb *c* connected with the tube *a* (Fig. 1), the latter having previously been completely filled with pure and perfectly dry xylene; the dropping-funnel *d*, which is connected by a gas-tight glass joint at *f*, is now connected and all of the air expelled from it and from the stem by addition of xylene and repeated shaking. Acetone of any dilution required can now be added through *d*, while the gas passes from *c* and collects in the tube *a*. After the reaction is complete a pressure-bottle is connected with *e*, the dropping-funnel is removed and the tube stoppered at *f*. The whole apparatus is now inverted and the hydrogen is forced from *g* through a washing-train[1] from which the air has previously been expelled by a current of pure carbon dioxide entering at *b*, and it is finally collected over caustic potash in an ordinary Schiff's azotometer. The quantity of hydrogen liberated was determined after each
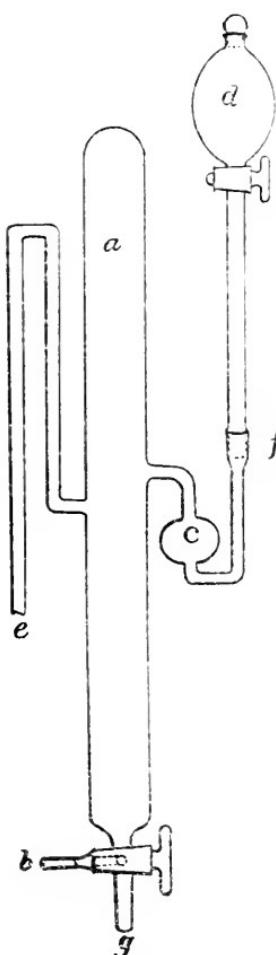
[1] The washing-train consisted of three Geissler potash-bulbs and a long tube filled with shavings of solid paraffin. The first two potash-bulbs were charged with liquid paraffin, the third with conc. sulphuric acid. All of the xylene vapor and other organic matter is removed from the hydrogen by this means.

experiment by explosion in a Bunsen eudiometer;[1] it was not necessary, therefore, to exercise the greatest care in expelling all air from the apparatus before collecting the gas.

The results of five determinations, with successively increasing dilution of acetone, are given in the following table; as the others, as a rule, agreed very well with the ones given below, it was not deemed necessary to take up space by adding more.

	Quantity of Sodium.	Proportion.	Found, Hydrogen.	Calcu- lated.	Percent- age.
I.	0.1078 gram.	Undiluted acetone added to apparatus filled with xylene.	3 cc.	52.1 cc.	5.77
II.	0.0990 "	Equal parts of acetone and xylene.	11.7 "	47.8 "	24.5
III.	0.1000 "	1 acetone : 5 xylene.	13 "	48.3 "	26.9
IV.	0.1054 "	1 : 25	25.93 "	50.7 "	51.16
V.	0.1078 "	1 : 100	32.71 "	52.1 "	62.7

These experiments furnish the final proof that acetone when treated with sodium in reality liberates hydrogen. As has been remarked before, the entire quantity of gas, if the acetone be pure, is used for purposes of reduction; the amount which is set free, however, increases with increasing dilution until it reaches a maximum at a ratio of about 1 : 100. At this point the action becomes quite slow, so that the sodium requires at least a week for complete disappearance. If the relative quantity of diluent is made still greater the formation of sodium acetone goes on so slowly that secondary reactions render the results inaccurate, if indeed the sodium is attacked at all after the first few minutes. It seems improbable, therefore, that the theoretical quantity of hydrogen can be obtained;[2] nor indeed is this at all necessary, as the main fact *that hydrogen is really set at liberty* is the only one of vital importance.

[1] A small ball of solid potash was thrust into the gas space after each explosion, in order to detect any carbon dioxide which might be present; the figures given belong only to determinations in which no contraction, owing to carbon dioxide, took place.

[2] In my former paper I stated that the theoretical quantity of hydrogen can in reality be obtained; the determinations referred to at that time were, however, made with very volatile petroleum ether as a diluent, the apparatus used was not perfectly adapted to the purpose, nor was care taken to determine the absolute quantity of hydrogen by explosion after each experiment.

*The Products which are formed by the Action of Sodium on
Acetone.*

If finely powdered sodium is covered with a great excess
of absolute ether, and acetone (purified as indicated above, and
also diluted with five times its volume of ether) is then gradually
added, reaction begins at once, hydrogen passes off and, after a
while, the ether comes to a boil, while at the same time a white,
flocculent substance, having somewhat the appearance of precipi-
tated aluminium hydroxide, separates. When this body is brought
in contact with the air it instantly assumes a deep red color and is
decomposed ; for that reason all operations in which it is con-
cerned must be conducted in an atmosphere of pure hydrogen
carefully dried with phosphoric anhydride. In order to obtain
the sodium compound in any desired quantity[1] I made use of the
apparatus described below.[2]

A flask, *a*, of 750 cc. capacity, having a flat bottom and wide
neck, was fitted with a quintuple-bored rubber stopper. Pure
hydrogen can be passed by means of the double-bored stop-
cock *d* at will, either through *a* or through *b*, which latter flask
is intended to contain the pure and dry ether necessary for
washing the precipitate when it is collected in the funnel *f*, into
which the products formed in *a* are aspirated by a Chapman
pump attached to *c*. The substances after being collected in *f*
are by suction freed from liquid as much as possible and then
repeatedly washed with the ether which is forced over from *b*, and
finally the remaining traces of the latter liquid are removed by
passing a rapid current of dry hydrogen through the apparatus
for more than an hour.[3] If it is found necessary to isolate products
which are soluble in ether, a second flask, similar to *b* (but contain-
ing a triple-bored rubber stopper, the third hole of which is con-

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[1] In my former paper I stated that the sodium compound was rapidly filtered, washed with
absolute ether and then dried on a porous plate in an atmosphere of hydrogen. Some redden-
ing always took place during the operation and, furthermore, the quantity of acetone sodium
isolated at one time was so small that I was compelled to be satisfied with a sodium determi-
nation and with the mere qualitative proof that acetone was produced from it by the addition
of dilute acids.

[2] I wish to take this opportunity of thanking Mr. R. R. Putnam for his suggestion of the
apparatus which was used.

[3] Of course all of the air must be expelled from the apparatus by means of a current of hydro-
gen, before the acetone is brought in contact with the sodium. The rapid escape of the gas
through the Liebig condenser, and consequent introduction of air, is prevented by closing the
end of the latter instrument by means of a mercury valve. The liquid is kept constantly
stirred during the reaction, by means of the rod *g* which is attached to a small water-motor.
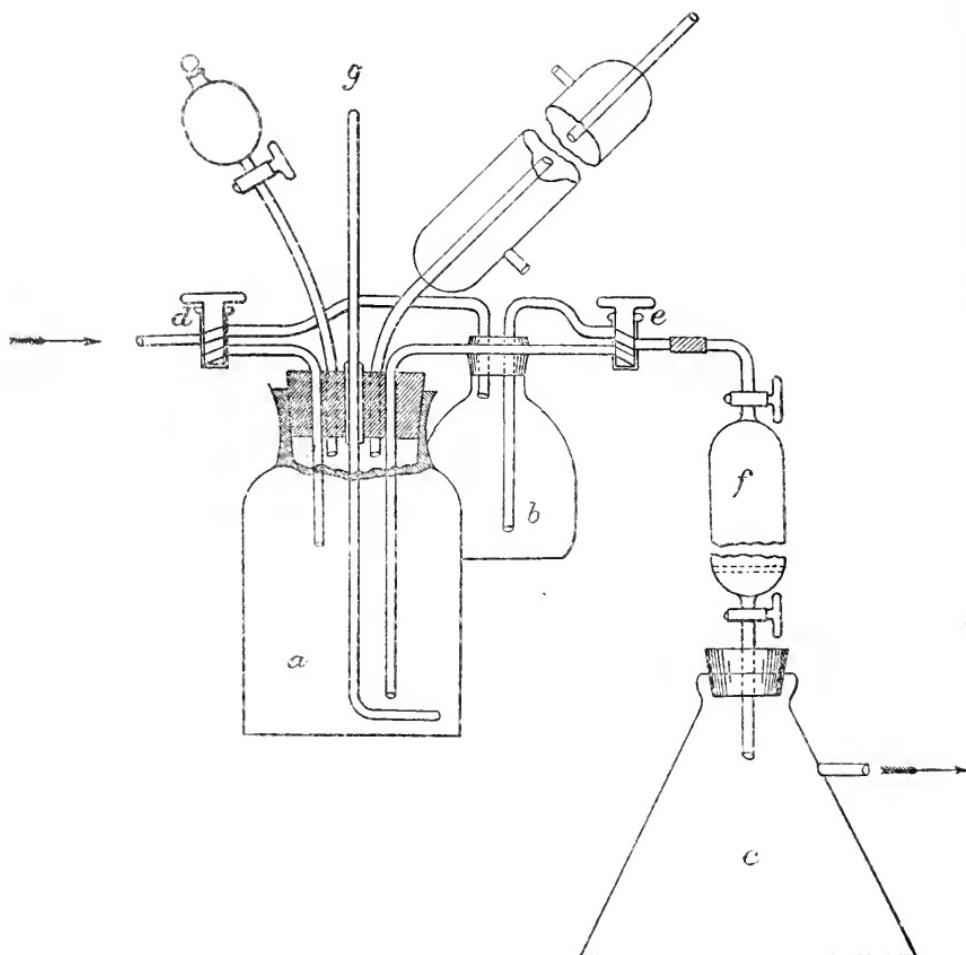
Fig. 2.

nected with a worm condenser), is introduced between *a* and *f*. If the precipitate in *a* is allowed to settle, the supernatant liquid can then be sucked over into this additional receiver, which operation may be repeated as often as necessary by successive additions of ether through the dropping-funnel. The dissolved products are finally isolated by gently heating and so evaporating the solvent. The funnel-cylinder *f* is closed above and below by means of glass stopcocks, so that when the latter are closed the precipitate can be removed and weighed without at any time being allowed to come in contact with a trace of air. As the research advanced it became apparent that the sodium compounds

produced were of two kinds, namely, those soluble and those insoluble in ether ; so that the separation of the two became of vital importance. The soluble portion, when pure, is a yellowish powder which instantly reddens when brought in contact with the air, the oxidation sometimes being so violent that the entire mass takes fire ; the insoluble part, on the other hand, is white, and when thoroughly washed shows much less tendency to change.

The Products of the Action of Sodium on Acetone which are Insoluble in Ether.

Several sodium determinations of samples of the insoluble portion were made ; these invariably demonstrated that a slight excess of sodium above the amount which is required by theory to be present in acetone sodium, was to be found.[1] The proportion of the metal is, however, always very nearly that which would be found in combination provided one atom of sodium were to react with one molecule of acetone, and from this it follows that if the sodium compound is in reality a mixture, and if *sodium pinakon is present* in this mixture, the latter substance must exist as the disodium derivative. The calculated percentage of sodium in pure sodium acetone is 28.75 per cent. I found in the insoluble portion of the products of the reaction 30.6, 31.42 and 31.2 per cent.[2] The excess of sodium is undoubtedly due to some decomposition which takes place, even if the entire work has been conducted in an atmosphere of pure hydrogen ; that this is probably the case is shown by the fact that those samples which had suffered some delay during their preparation were always the ones which contained relatively the greatest quantity of sodium.

In order to identify the substances which are present in the insoluble sodium compound, ten samples of the product, entirely free from ether or acetone, each prepared by treating 2.5 grams of finely powdered sodium with an excess of well diluted acetone,[3]

[1] Beckmann [Ann. Chem. (Liebig) **266**, 19] found that the sodium contents of acetophenone sodium was always about 2.5 per cent. *less* than the calculated quantity. This investigator also states that no permanent gas is developed when sodium acts on acetophenone ; if all of the hydrogen were used for purposes of reduction it would follow that the quantity of sodium would be less than the theory demands.

[2] These figures are selected from a number of analyses which gave similar results.

[3] Great care was taken thoroughly to remove all acetone from these samples by several decantations with pure ether before sucking the precipitate into the glass-tube filter (*f*, Fig. 2), and then by washing the collected precipitate repeatedly with the same liquid. The current of hydrogen was then passed through the filter until absolute certainty was reached that every trace of liquid had been evaporated.

were, as soon as the reaction was complete, treated with a slight excess of very dilute ice-cold acetic acid ; this instantly dissolved the substance, the solution being of a light straw-color and only very slightly turbid. All of the acidified portions of liquid were now united, neutralized and distilled until no iodoform reaction could be obtained with a sample of the residue in the retort. The distillate was then supersaturated with potassium carbonate, again distilled, and this operation repeated until only about 75 grams of fluid were left, which, upon addition of the same solid, separates into two layers, the lower one a colorless solution, the upper one a straw-colored oil. The latter was allowed to stand over solid potassium carbonate, and was then carefully fractioned, with the following result : about one-half passes over between 65° and 83° ; the thermometer then rapidly rises to 165°, between which temperature and 190° the greater part of the remainder distils, while the few drops of residue boil between 200° and 220°.

The low-boiling portion was now carefully treated with a concentrated solution of sodium bisulphite, upon which addition the entire mass apparently solidifies into the characteristic shiny plates of acetone sodium bisulphite. When, however, these crystals are pressed out, a considerable quantity of mother-liquor separates, the latter forming two layers, the lower one of which is an aqueous solution of acetone sodium bisulphite, the upper one an organic liquid. This liquid was separated and dehydrated by first distilling it several times over solid potassium hydroxide, and then by repeatedly fractioning, after the addition each time of a small piece of sodium. The entire quantity then boils between 81° and 81.5° (739 mm. pressure) and gives the following analytical data :

I. Twice fractioned over sodium—

Substance, 0.2038 gram ; CO_2, 0.4290 gram ; H_2O, 0.2380 gram. Found : $C = 57.5$; $H = 12.92$ per cent.

II. Three times over sodium—

Substance, 0.2230 gram ; CO_2, 0.4764 gram ; H_2O, 0.2653 gram. Found : $C = 58.4$; $H = 13.16$ per cent.

III. Four times over sodium[1]—

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[1] The sodium evidently first in greater part attacks the ethyl alcohol to form sodium thylate, and so, after repeated additions of this metal, and fractioning, only isopropyl alcohol is left behind. Pure isopropyl alcohol which has been treated in this way is *almost entirely* indifferent to sodium at ordinary temperatures, sodium isopropylate being formed *only when the liquid is warmed.* The question whether sodium does or does not attack a given substance, therefore, has no bearing on the question as to whether that substance contains an hydroxyl group or not.

Substance, 0.2550 gram ; CO_2, 0.5586 gram ; H_2O, 0.3102 gram.
Found : C $=$ 59.75 ; H $=$ 13.43 per cent.

Calculated for Isopropyl Alcohol.		Calculated for Ethyl Alcohol.	
C	60. per cent.	C	52.17 per cent.
H	13.3	H	13.17

These analyses prove, without doubt, that the isopropyl alcohol which was produced by reduction was mixed with some *ethyl alcohol;* however, as the acetone used was from the sodium bisulphite compound, and as the solvent was ether which was entirely free from alcohol, there is only one interpretation of the facts possible, namely, that ether is *not* an absolutely indifferent solvent in this and similar reactions.[1] I have repeated the above experiments several times and always with the same results. This conclusion is also borne out by the work with benzoyl chloride which is given below.

The filtered acetone sodium bisulphite which was separated from the isopropyl alcohol, was treated with a concentrated solution of sodium carbonate and fractioned ; the entire quantity of the organic liquid which separated then boiled at 56.5° and proved to be pure acetone. The relative quantities of acetone and of isopropyl alcohol formed vary with the amount of ether which is originally employed as a solvent ; under most favorable circumstances there is about twice as much acetone as isopropyl alcohol ; under the most unfavorable, about equal quantities.

The fraction of the anhydrous distillate boiling between 165° and 190°, obtained from the decomposition of the insoluble sodium compounds by dilute acetic acid, was mixed with about three times its own volume of water and allowed to stand. The liquid soon becomes quite hot, and upon cooling solidifies to a mass of crystals which contains a few drops of a yellow oil ; the latter was removed by washing with a little ether, while the solution thus obtained was united with the fraction boiling between 200° and 220°. The solid was now recrystallized from a little hot water, from which on cooling it separates to the last trace in large, transparent, quadrangular plates which effloresce in the air and finally evaporate at ordinary temperatures. These qualities are

[1] Absolutely pure ether, which apparently has no effect on sodium, will nevertheless be attacked by the metal after some time if placed in the sunlight. Ether over sodium should therefore be kept in the dark. (See also Beckmann : Ann. Chem. (Liebig) **266**, 9.)

so characteristic of hydrated pinakon that an analysis was deemed unnecessary.[1]

The high-boiling portion (between 200° and 220°) was finally fractioned, when it was found that the greater portion passes over between 206° and 212°, while a very small amount of a tar-like residue remained in the flask. This yellow oil is undoubtedly, in part, identical with the high-boiling phoron which was obtained by Fittig[2] by the action of quicklime on acetone, and by Städeler[3] when he treated the same substance with sodium, and which was subsequently compared by Kachler[4] with phoron obtained by other means, and described in his table comparing the properties of compounds having the formula $C_9H_{14}O$. However, my oil reacts only slowly and very incompletely with phenylhydrazine; evidently, therefore, there is only very little ketone present,[5] in comparison with a large quantity of a reduced body, but, as the amount of this reduced body, even after uniting the product of several operations, was not sufficient to warrant a careful separation, no analysis was made.[6] Mesityl oxide could not be found among the products produced by acidifying the sodium compounds.

That portion of the product of the action of sodium on acetone which is insoluble in ether consists, therefore, of *acetone sodium*, *sodium isopropylate*, and *disodium pinakonate* mixed with a small quantity of sodium ethylate. If the ether used in the initial operation is sufficient in quantity, then the greater part consists of acetone sodium, while sodium isopropylate and disodium pinakonate are present in about equal proportions.[7]

[1] The crystals were also converted into anhydrous pinakon by distillation over solid caustic potash; the oil so obtained possessed the very characteristic odor of anhydrous pinakon.

[2] Ann. Chem. (Liebig) **110**, 32.

[3] *Ibid.* **111**, 279.

[4] *Ibid.* **164**, 80.

[5] Perhaps it is $C_{12}H_{20}O$ (boiling-point 213° to 217°), formed by reducing mesityl oxide. *Vide* Claisen: Ann. Chem. (Liebig) **180**, 8.

[6] Only about 0.75 gram of this high-boiling body can be obtained by decomposing 30 grams of the sodium compounds.

[7] Beckmann and Paul (Ann. Chem. (Liebig) **266**, 18) believe that the sodium derivative of acetophenone is produced by two molecules of the latter substance reacting with two atoms of sodium, and assign to the sodium derivative an improbable formula which differs from that of disodium acetophenone-pinakon only in having one sodium atom attached to carbon instead of replacing a hydrogen atom in hydroxyl. They assume this more complicated structure to exist because no hydrogen is evolved during the reaction between sodium and acetophenone. In the case of acetone, however, hydrogen *is* evolved; the assumption that acetone sodium has a molecular formula which is double that which the simplest relationship calls for, is therefore unnecessary. Nevertheless, it is not impossible that *pinakon sodium* is not present in the

The Sodium Compound Soluble in Ether.

As has been mentioned above, there remains a yellow powder, which is oxidized with remarkable readiness, after completely evaporating the ether and acetone from the ethereal solution of the soluble sodium compound. In order to ascertain the nature of this compound, the product of each operation, as soon as finished, was acidified with ice-cold and very dilute acetic acid, and the liquids produced by ten such decompositions were united. As soon as the dilute acid came in contact with the powder, the latter dissolves and at the same time assumed a deep red color, which changed to yellow when an excess of acid had been added, while a brownish colored oil separated.[1] The solution, after the removal of the oil, gave an iodoform-reaction with iodine and ammonium iodide, so that the presence of acetone therein was beyond doubt.[2] The oil was isolated, dried over calcium chloride

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sodium compounds, for the pinakon may be only produced upon acidifying. A sodium compound having the structure

$$\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ C-ONa & C-ONa \\ |\overline{}\,-\,\overline{}| & C-CH_3 \\ | & CH_3 \\ | & | \\ CH_2 & C-ONa \\ \overline{} & C-CH_3 \end{array}$$
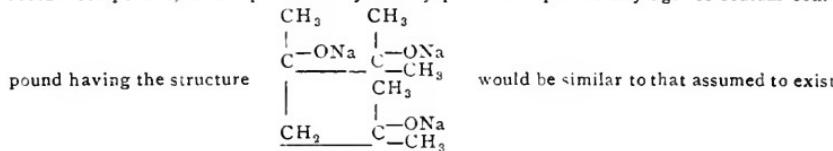
would be similar to that assumed to exist in the case of acetophenone sodium ; one molecule of this substance might break down into one of pinakon and one of acetone when an acid is added. Such a theory is doubtful, however, because such a body would, presumably, be stable when acidified. Although its formation by addition to the unsaturated pair of carbon atoms in acetone sodium is not improbable, it may be present in the high-boiling portions. The fact that one portion of the sodium compounds derived from acetone is *soluble*, the other *insoluble*, shows that two different classes of such compounds are produced by the reaction, and, as the pinakon in conjunction with acetone always appears on acidifying the *insoluble* portion, it seems necessary to assume that a more complicated sodium compound exists in this part. The evolution of the large quantity of hydrogen during the reaction shows beyond doubt, however, that the greater portion of the sodium acetone is present in its simplest form, and this, most probably, in the soluble part.

[1] The ether-soluble compound is also instantly decomposed by water, the solution assuming a deep red color, while an oil, which is also red, separates. On acidifying, the solution changes to yellow and the oil to brown.

[2] During the course of this research I took occasion to review the various qualitative methods for proving the presence of acetone when mixed with isopropyl alcohol and pinakon. The usual iodoform-reaction in which sodium or potassium hydroxide is used is, of course, out of the question, as both isopropyl alcohol and pinakon would yield iodoform under similar circumstances. The acetone-test with precipitated mercuric oxide is also of no value when the presence of small quantities of acetone is to be proven, because mercuric oxide is noticeably soluble in caustic alkalies, and this solution, after acidifying, gives a very marked turbidity with stannous chloride ; the solubility of the oxide is, however, not increased by the presence of isopropyl alcohol or pinakon. On the other hand, the iodoform-reaction with iodine and an ammoniacal solution of ammonium iodide (Gunning: Ztschr. anal. Chem. **24**, 147) is very satisfactory. Neither isopropyl alcohol nor pinakon forms iodoform with this mixture, even if in contact with it for days ; while acetone reacts after a very few minutes, even when very dilute. It must be remembered, however, that the condensation-products of acetone likewise produce iodoform when treated with this reagent. The formation of indigo with orthonitrobenzaldehyde is not always practicable, and the benzalacetone-reaction cannot be used to prove the presence of small quantities.

and fractioned: a small portion passed over between 100° and 140°; the thermometer then rose rapidly until it reached 200°, between which temperature and 220° about one-third of the remainder distilled; a considerable portion then boiled between 220° and 290°, the residue in the flask being a perfectly solid semi-transparent resin. The portion distilling between 200° and 220° was now refractioned under diminished pressure, the greater part boiling at 165° (90 mm.)[1]; the middle part of this fraction was analyzed:

Substance, 0.1793 gram; CO_2, 0.5145 gram; H_2O, 0.1788 gram.

	Calculated for $C_9H_{14}O$.	Found.
C	78.26	78.26
H	10.19	10.9

There is no doubt, therefore, that this portion of the oil possesses the formula $C_9H_{14}O$, and from its boiling-point and other properties it must be considered as being identical with phoron which is produced by the action of alkaline condensing-agents on acetone. As might be expected, this substance reacts readily with phenylhydrazine, and the same is true of the high-boiling portion (220°–290°), although no body with even an approximately constant boiling-point could be isolated from this part.

The acid solution which was obtained by treating the ethersoluble sodium compounds with dilute acetic acid and from which the oil above described had been separated, was neutralized with potassium carbonate and then treated exactly as has been described above in that portion of this article referring to the isolation of acetone and isopropyl alcohol from the solution obtained by similarly acidifying the insoluble portion. When the organic liquid had been entirely separated and freed from water it was fractioned: a small quantity passed over between 60° and 70°, and this part completely united with sodium bisulphite to form acetone sodium bisulphite. The higher-boiling portions consisted of mesityl oxide and a little pinakon. The organic liquids which can be separated from the aqueous solution are much less in quantity than is the oil described above, and it will be noticed that *no isopropyl alcohol* and but very little pinakon can be found among

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[1] This fraction boils between 206° and 212°, ordinary pressure. My experience is identical with that of Fittig when he investigated the high-boiling products from the action of quicklime on acetone, and of Städeler when he produced the same body from sodium, namely, no substance with a perfectly constant boiling-point could be isolated.

the products of the decomposition by dilute acids of the sodium compounds which are soluble in ether, they being almost exclusively *condensation-products of acetone.*

There can scarcely be any doubt that the ether-soluble portion of the sodium compounds represents almost pure sodium acetone, and that the mesityl oxide, phoron and higher-boiling oils which are found after adding the acid, are produced by the intensely energetic action which takes place when the dry sodium acetone is acidified. That this is the case is shown by the fact that the dilute ethereal solution of this substance, after it is carefully acidified, contains only a very small quantity of mesityl oxide and no phoron ; neither has the latter of these products ever been observed among the results of the action of chlorocarbonic ether or of benzoyl chloride on acetone sodium.[1]

The ether-soluble and -insoluble portions appear, when the work is carefully conducted, in about equal proportions; if the amounts of each which were produced in any one operation are added together, then, assuming that the ether-soluble portion is almost pure acetone sodium, the quantity of the latter body by far exceeds that of the sodium isopropylate and pinakonate.

The experiments detailed above show without doubt that a molecule of acetone contains a hydrogen atom which is replaceable by sodium, and, this point being settled, the next question to be solved is in regard to the structural formula of the sodium compound—whether the metal is attached to oxygen or to carbon. At first, as was described in a former paper,[2] I studied the action of ethyl chlorcarbonate on acetone sodium, but, as the reaction led to much more complicated results than the ones which I then supposed to be the true ones, I next chose benzoyl chloride, and indeed the latter reagent led to the most complete clearing-up of the case. For this reason I shall give a detailed description of the work with benzoyl chloride, reserving a short mention of the reactions with chlorcarbonic ether for the close of this article.

The Action of Benzoyl Chloride on the Products of the Reaction between Acetone and Sodium.

Three grams of finely powdered sodium are covered with 300 cc. of absolute ether and placed in the flask *a* of the apparatus

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[1] That this is the case was shown in my former article on this subject : This Journal **13**, 321.

[2] Freer and Higley : *Ibid.* **13**, 322.

(Fig. 2) ; all of the air is then expelled by hydrogen, and an excess of diluted acetone gradually run in until all of the sodium has disappeared, the whole being meanwhile vigorously stirred by the water-motor. Somewhat less than the calculated quantity of pure benzoyl chloride—entirely free from benzoic acid and diluted with twice its own volume of ether—is then slowly dropped in : an instant and most violent reaction takes place and the ether comes to a boil (so that it is necessary from time to time to cool the flask with water) while at the same time the sodium compound assumes an orange color. After all of the benzoyl chloride has been added the whole is warmed for about an hour on a water-bath ; the reaction is completed when the orange color has changed to the pure white of sodium chloride. The ethereal solution is then of a light straw-color. The results of ten such operations are united into one and worked up together. The whole is first shaken out several times with water and is then extracted with a solution of sodium bicarbonate until a sample of the latter separates nothing when acidified. The remaining fluid is then treated in the same way with sodium carbonate and finally with 10-per cent. sodium hydroxide ; the extractions with each reagent are preserved and investigated separately.

The Portion of the Oil which is Insoluble in Alkalies.

The neutral products of the reaction which are now alone present in the ethereal solution are dried over fused calcium chloride, the ether evaporated, and the remaining brown oil, which possesses an odor resembling benzoic ether, is fractioned. The first distillation separates the fluid into a low-boiling portion ($128°–133°$) and a part passing over above $200°$, while a high-boiling residue which decomposes on distillation remains in the retort. The oil boiling between $128°$ and $133°$ is mesityl oxide, mixed with a small quantity of a chlorinated body which it is impossible to separate by fractional distillation.

The product boiling above $200°$ was now carefully fractioned under diminished pressure ; after a few drops of remaining mesityl oxide have been removed the thermometer rises rapidly to $137.5°$ (80 mm.), and between this temperature and $139°$ almost the entire quantity passes over.[1] The distillate is a colorless or very slightly

[1] The boiling-points of this oil are as follows : $114°$ at 20 mm., $120°$ at 39 mm., $135°$ at 69 mm., $137.5°$ at 83 mm.

yellow-colored oil, with a high refractive index and an ethereal odor somewhat resembling that of ethyl benzoate; *it does not react with phenylhydrazine, and instantly adds bromine in the cold* without liberating hydrobromic acid. Owing to the constant boiling-point and the further properties of this oil there seemed scarcely any doubt that a benzoic ester of β-allyl alcohol was present, but, nevertheless, the analyses (with the single exception of that of one of several preparations) indicated that this presumably uniform body was in reality a mixture:

	Calculated for $C_6H_5.CO_2.C.CH_3.$ $\overset{\parallel}{C}H_2$	For $C_6H_5.CO_2.C.CH_3.$ $\overset{\vert}{C}H_3$	For $C_6H_5.CO_2 C_2H_5.$
C	74.07	73.23	72.00
H	6.17	7.36	6.66

	I.	II.	III.	IV.
		Found.		
C	73.63	72.92	72.86	72.66
H	6.09	7.76	7.84	7.93

These numbers, with the exception of those in the first analysis, agree with those which would be expected were a mixture of the benzoic esters of β-allyl alcohol, isopropyl alcohol and ethyl alcohol;[1] a separation by means of fractional distillation is, however, impossible, because the boiling-points of the substances in question lie too near together, as I proved by distilling in separate flasks isopropyl benzoate, ethyl benzoate, and the oil undergoing investigation, all at the same time and attached to the same manometer: the isopropyl ester boiled at 119°, the ethyl ester at 116°, and the product of the action of benzoyl chloride on acetone sodium at 120° (pressure 39 mm.). In order, therefore, definitely to determine the nature of the body under discussion I decided to saponify the oil and to identify the products formed by this means. Nine grams of the oil were mixed with a slight excess of 5-per cent. caustic potash solution (calculated for β-allyl benzoate) and then boiled for eight hours in a flask attached to an inverted condenser fitted with a mercury valve; after that time the ethereal odor had disappeared and the weight of oil diminished to 2 grams. The latter was separated from the alkaline solution, dried over

[1] Probably a trace of the product of the reduction of mesityl oxide, $C_{12}H_{20}O$ (boiling-point, 213°-217°), is also present; this would increase the proportion of hydrogen very much. No condensation-products of acetone are mixed with this oil, *for it does not react with phenylhydrazine.* Some analyses were obtained in which the hydrogen was as low as 7 per cent., but these are not given because, to make a perfectly fair representation, the above four sets of numbers were selected simply in the order in which the analyses were made.

potassium carbonate and fractioned. A few drops distilled between 120° and 134° and were evidently mesityl oxide; the thermometer then rapidly rose to 200°, between which temperature and 220° the whole of the remainder passed over. This high-boiling portion is identical in odor and other properties with the phoron which had previously been obtained ; *it readily reacts with phenylhydrazine.* These condensation-products were evidently produced from acetone by the action of caustic alkali ; the acetone, in turn, being the result of the saponification. That no such bodies were present in the original oil is abundantly proven by the fact that it does not react with phenylhydrazine, and further, by the vapor-density, which agrees quite closely with that predicted by theory.

Vapor-density of oil boiling at 114° (20 mm.), Hoffmann apparatus ; vapor of aniline :

Weight of substance, 0.0442 gram, $V = 146$ cc., $h = 494.4$ mm., $t = 184.5°$, $h' = 76$ mm., $t' = 24°$, $B = 745$ mm. ($t = 18.5°$).

D — Calculated for $C_6H_5COOC — CH_2 = 5.61$; Found $= 5.51$.

$$\underset{\parallel}{}\;\overset{}{CH_2}$$

The alkaline solution left from this saponification was now acidified with dilute sulphuric acid, the precipitated benzoic acid filtered out and the acid solution supersaturated with potassium carbonate, distilled, the distillate treated in the same way, and so on until the separated organic liquid became anhydrous. No acetone was present in the substance so isolated, as was proven by the addition of sodium bisulphite ; the liquid was therefore once more distilled over potassium carbonate, and finally dehydrated by repeated fractioning, with the addition of a small piece of sodium before each operation. The boiling-point was then 81.5° and the analyses as follows :

I. Twice distilled over sodium : $C = 57.69$, $H = 13.29$ per cent.

II. Three times distilled over sodium : $C = 58.73$, $H = 13.3$ per cent.

Calculated for $CH_3.CHOH.CH_3$: $C = 60$, $H = 13.3$ per cent.

Evidently a mixture of isopropyl alcohol and ethyl alcohol, similar to that obtained by acidifying acetone sodium, was present, and if it had been deemed necessary, the ethyl alcohol could have been entirely removed by continued distillations over sodium. This saponification proved, therefore, that the oil undergoing investigation was in reality a mixture of the benzoic esters of

isopropyl, ethyl and β-allyl alcohols; the acetone, which it was expected to isolate, was, however, converted into the high-boiling condensation-products of that body—in all probability the more easily because of its being liberated from its ethereal combination, as it were, in the nascent state. Although the mesityl oxide and the phoron which were obtained could have no other origin than the one referred to, it would nevertheless be more satisfactory to obtain the pure acetone by saponification, and in order to accomplish this result, hydrolysis by means of dilute hydrochloric acid was next attempted. Twelve grams of the oil, with an excess of 5-per cent. hydrochloric acid, were sealed in tubes and heated at 150° for forty-eight hours; the oil had then entirely disappeared and considerable pressure had been developed, as was shown on opening the tubes.[1] The acid liquid, after the benzoic acid had been removed, was supersaturated with potassium carbonate and then distilled, the distillate treated in the same way and so on, until the organic fluid, which was dissolved, was rendered anhydrous. *The entire quantity then boiled between* 60° *and* 85°. Two fractions of this liquid were taken, one boiling below and the other above 73°; the lower portion, which was about twice as great in volume as the other, was carefully treated with a saturated solution of sodium bisulphite, whereon the entire quantity solidified in the form of the characteristic shiny plates of acetone sodium bisulphite. Subsequently, pure acetone was obtained from this compound by heating with sodium carbonate. The liquid boiling above 73° also contained some acetone, but a large part was isopropyl alcohol mixed with a little ethyl alcohol. These results prove that by saponifying the neutral oil obtained by the action of benzoyl chloride on acetone sodium, *acetone*, isopropyl and ethyl alcohols can be isolated, in addition to benzoic acid. There can be no doubt, therefore, that acetone sodium, when treated with benzoyl chloride, yields a true ester of benzoic acid and that this ethereal salt is β-allyl benzoate, $C_6H_5COOC - CH_3$. The saponi-

$$\overset{||}{CH_2}$$

fication takes place according to the following equation:

$$C_6H_5.COO.C.CH_3 + H_2O = C_6H_5.COOH + CH_3.COH : CH_2.$$
$$\overset{||}{CH_2}$$
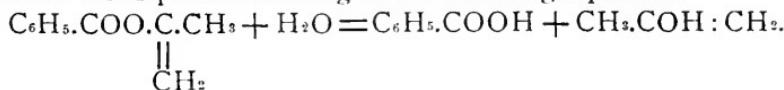
[1] The escaping gas burns with a strongly luminous flame, and a portion, collected over water, absorbs bromine even when the daylight is nearly excluded. It is probably allylene, although this supposition is given with considerable doubt, as benzoic isopropyl ester may break down into benzoic acid and propylene under similar circumstances. This question must be the subject of future investigation.

If ordinary acetone in reality contains a carbonyl group, then the β-allyl alcohol changes to CH_3—CO—CH_3 as soon as it is liberated ; but if, on the other hand, free acetone is an unsaturated alcohol, then no further change need be considered. I shall not, at the present time, commit myself to either opinion, as the work which I have undertaken with the hope of settling the constitution of acetone is not, as yet, completed.

The Portion of the Oil which is Soluble in Alkalies.

As was mentioned in the above, the ethereal solution which was obtained as a product of the action of benzoyl chloride on acetone sodium was successively treated with aqueous sodium bicarbonate, sodium carbonate and sodium hydroxide, and the yellow to red colored solutions so obtained were then each worked up separately. Benzoic acid is almost exclusively separated on acidifying the bicarbonate solution with dilute sulphuric acid, and indeed this substance is formed in such quantity that its production is, undoubtedly, an essential part of the entire reaction. It seems as if the quantity of benzoic acid is in direct proportion to the amount of mesityl oxide which is formed.[1]

The results with the sodium-carbonate solution are entirely different; when the latter is acidified there separates a red, semisolid mass which yields *acetophenone*,[2] acetic acid and benzoic acid when it is distilled. It follows from this fact that ketones produced by the substitution of one or more hydrogen atoms in an acetone molecule by benzoyl chloride were present before distillation. The red precipitate which is obtained on acidifying with

[1] The formation of mesityl oxide is peculiar to this reaction with benzoyl chloride, but very little mesityl oxide is found in the substances isolated by direct acidification of acetone sodium, or in the products of reaction between that substance and ethyl chlorcarbonate. That the mesityl oxide is not due to the action of benzoyl chloride on the excess of free acetone is proven by the fact that the two substances can be left in contact for weeks with but very little condensation. When I first tried the action of benzoyl chloride on acetone sodium I extracted the ethereal solution with 10-per cent. sodium-hydroxide solution from the very beginning, and it then seemed to me as if the benzoic acid might be due to the saponification of an extremely unstable ester. However, the quantity of acid is as great if extraction with sodium bicarbonate is resorted to ; it is always about 10 per cent. of the total quantity of benzoyl chloride (calculated in terms of benzoic acid) which was used. The benzoic acid also appears if no attempt is made to extract with alkalies, the ethereal solution being fractioned without further preliminaries, or if the same be distilled in a current of steam. In spite of all these considerations the most probable explanation seems to be that the benzoic acid is due to the saponification of an unstable ester.

[2] The acetophenone was separated by careful fractioning, as an oil boiling at 202°; it was identified by its characteristic odor, by a combustion, and finally by the formation of its compound with phenylhydrazine (melting-point 105°).

dilute sulphuric acid—in quantity it is about 8 grams for every
120 grams of benzoyl chloride used—was treated as follows, in
order to isolate the substances contained therein: It was dissolved
in the least possible quantity of 10-per cent. sodium-hydroxide
solution, and carbon dioxide was then passed into the solution
until no further precipitate separated. The resulting yellowish,
flaky body was then filtered out and dissolved in the least possible
quantity of hot absolute alcohol; when this solution is left for
crystallization there separates a small quantity of fine, white
needles, soluble in alcohol with difficulty, and melting at 213°.[1]
These are filtered and the remaining mother-liquors allowed to
stand. Long prisms then gradually form, and are separated when
they no longer increase in quantity. They are then powdered,
spread on a porous plate, and finally repeatedly recrystallized
from the least possible quantity of alcohol. When entirely pure
this body forms long, quadratic, needle-like prisms, which are
soluble in alcohol, soluble with difficulty in ligroïn; when heated,
they soften (if not entirely pure) at 78°, but do not melt until
100°–101° is reached. These properties agree completely with
those found for dibenzoylacetone,[2] and analysis proved that the
latter body is in reality produced:—

I. Substance, 0.1829 gram; CO_2, 0.5126 gram; H_2O, 0.0927
gram.

II. Substance, 0.1143 gram; CO_2, 0.3233 gram; H_2O, 0.0580
gram.

	Calculated for $C_{17}H_{14}O_3$.	Found.	
		I.	II.
C	76.7	76.43	77.00
H	5.38	5.63	5.61

[1] This body is not very readily soluble in sodium carbonate, and it is therefore, in greater part, to be found in the high-boiling residue left in the retort after distilling the neutral oil. It will therefore be referred to again in a subsequent paragraph.

[2] Alexander B. Smith: Inaugural Dissertation, Munich, 1889, page 30. This author prepared dibenzoylacetone by the action of benzoyl chloride on sodium benzoylacetone. He ascribes the softening of the crystals at 78° to the presence of an isomeric body. I have found that dibenzoylacetone, if recrystallized a sufficient number of times, no longer softens at 78°; a body melting at 55° can, however, be separated from the last rests of the mother-liquors. The quantity of this substance which I have had at my command has been too little to allow me to hazard an opinion as to its nature. Whether it is an isomer of dibenzoylacetone, or whether it changes to ordinary dibenzoylacetone on recrystallizing, is yet to be determined. Claisen, in a paper (Ber. d. chem. Ges. **26**, 1879) which appeared while this article was being written, mentions that repeated crystallization changes the dibenzoylacetone (melting at 100°–101°) into an isomer melting at 109°–110°; I had not noticed this change with my dibenzoylacetone, even after recrystallizing nine or ten times. I have, however, as will be seen below, isolated another body which melts finally at 155°.

The crystals which were used in the first analysis changed the color of a solution of ferric chloride to an intense reddish purple; they probably, therefore, contained a trace of monobenzoylacetone, since this would decrease the percentage of carbon and increase that of the hydrogen.

The mother-liquors from the crystallization of dibenzoylacetone form a dark brown oil which possesses the very characteristic odor of monobenzoylacetone; if allowed to stand, part of this oil gradually solidifies, and the solid substance, when crystallized from 90-per cent. alcohol, deposits long needles having the characteristic appearance and odor of benzoylacetone. The melting-point of these crystals is 58° to 62°, and a comparison with a sample of benzoylacetone prepared by a different method [1] established their identity; the alcoholic solutions in both samples also assumed the same Bordeaux-red color when treated with a drop of a solution of ferric chloride. Owing to the very characteristic properties as well as to the difficulty with which the small quantities of benzoylacetone are to be separated from dibenzoylacetone, no ultimate analysis was made.

The High-boiling Residue which remains after distilling the Oil Insoluble in Alkali.

In spite of the fact that all of the alkali-soluble bodies have been removed before distillation, the residue which remains in the retort, and which is an almost black, tar-like mass, contains considerable quantities of benzoic acid, as well as some benzoylacetone. In order to remove these acid bodies the tar was once more dissolved in ether and then repeatedly extracted with 10-per cent. sodium-hydroxide solution; the ethereal solution was then dried over calcium chloride, the ether evaporated and the residue stood aside for possible crystallization. After some weeks a not inconsiderable quantity of a body which crystallizes in long, felt-like needles was deposited; this was separated from the remaining oil by being spread on a porous plate,[2] and was finally recrystallized from hot absolute alcohol. After this operation it became apparent that

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[1] I owe this sample to the kindness of Prof. J. U. Nef, whom I wish to take this opportunity of thanking.

[2] I have found the dried pulp which is to be obtained from paper factories, and which is rolled in large sheets about ¼ of an inch in thickness, to be much superior to porous plates as an agent for removing sticky mother-liquors. The drying action is much quicker and more complete.

there were in reality two bodies present; the larger portion is with difficulty soluble in alcohol, and separates from the latter solvent in asbestos-like needles which melt at 214°, while the minor part separates from the mother-liquors as a granular precipitate which melts at 156° to 157.5°.

The body melting at 213° was repeatedly crystallized, and then finally dried at 100° and analyzed:

I. Substance, 0.0786 gram; CO_2, 0.2250 gram; H_2O, 0.0442 gram.

II. Substance, 0.1737 gram; CO_2, 0.4999 gram; H_2O, 0.0772 gram.

	Calculated for $C_{20}H_{18}O_3$.	Found. I.	Found. II.
C	78.46	78.37	78.47
H	5.88	6.23	4.95

The body $C_{20}H_{18}O_3$ is in all probability obtained from benzoyl-acetone by the extraction of water, as the following equation will show: $2C_{10}H_{10}O_2 = C_{20}H_{18}O_3 + H_2O$; and it therefore may be dibenzoylmesityl oxide; whether it is formed from a sodium compound of mesityl oxide, or whether it is produced by condensation between two molecules of benzoylacetone, can naturally not be, as yet, decided.

In addition to the above there is found, as has been mentioned, another crystalline substance which is more soluble in alcohol, which separates from that solvent in short prisms having a melting-point of 156°–157.5°, and which gives the following numbers on analysis:[1]

Substance, 0.1715 gram; CO_2, 0.4767 gram; H_2O, 0.0014 gram.

	Calculated for $C_{17}H_{16}O_3$.	Found.
C	76.12	75.80
H	5.96	5.92

A body of the composition $C_{17}H_{16}O_3$ might be dibenzoylacetone after the addition of two hydrogen atoms, but all speculation as to whether such a substance is really under consideration would be premature at the present time.

The black, tar-like residue after all other substances have been separated shows no tendency toward further crystallization. It is decomposed on distillation, even in a vacuum, a large quantity of

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[1] I could obtain enough of the pure body for only one analysis.

gas passing off, while benzoic acid and a trace of acetophenone distil over, leaving as a residue in the retort a perfectly solid resin. An attempt at saponification gave equally unsatisfactory results : benzoic acid and an uninviting neutral tar being produced, so that, as a consequence, further investigation was abandoned.

The experiments which have been detailed above show, without doubt, that acetone, like acetoacetic ether and other bodies related thereto, contains a hydrogen atom which is capable of being replaced by sodium, while the fact that acetone sodium forms an ester when treated with benzoyl chloride—to which ester the structural formula : $C_6H_5.COO.C\diagup^{CH_3}_{\diagdown CH_2}$ must be assigned— also proves, beyond doubt, that the sodium atom in acetone sodium is combined with oxygen to form a natroxyl group. It is possible, therefore, when dealing with the sodium compound of a strongly positive substance such as acetone, to substitute the sodium directly by benzoyl, an experience which is doubtless contrary to the one which has been made with acetoacetic ether. The formation of benzoylacetone from sodium acetone and benzoyl chloride can therefore be explained only by the assumption that addition must first take place.[1] The simultaneous production of dibenzoylacetone is, in my opinion, most easily understood by applying the explanation which Nef[2] gives in his paper discussing the similar reactions taking place with acetoacetic ether. The first change consists in the addition of benzoyl chloride :

$$\text{I.} \quad \begin{matrix} CH_3 \\ | \\ CONa \\ || \\ CH_2 \end{matrix} + \begin{matrix} Cl \\ | \\ CO.C_6H_5 \end{matrix} = \begin{matrix} CH_3 \\ | \\ C\diagup^{ONa}_{\diagdown Cl} \\ | \\ CH_2.CO.C_6H_5. \end{matrix}$$
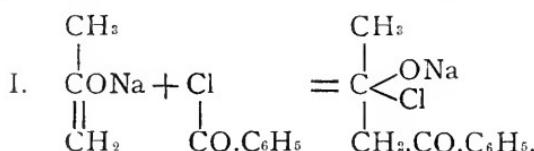
The latter body now separates hydrochloric acid, leaving sodium benzoylacetone :

$$\text{II.} \quad \begin{matrix} CH_3 \\ | \\ C\diagup^{ONa}_{\diagdown Cl} \\ | \\ CH_2.CO.C_6H_5 \end{matrix} = \begin{matrix} CH_3 \\ | \\ CONa \\ || \\ CH.CO.C_6H_5. \end{matrix} + HCl.$$
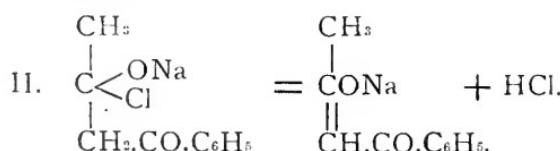
[1] The intense orange color which is produced as soon as benzoyl chloride comes in contact with sodium acetone may be due to the formation of such an addition-product.

[2] Ann. Chem. (Liebig) **266,** 61.

The liberated hydrochloric acid, of course, by preference will attack the acetone sodium, forming sodium chloride and free acetone; a lesser portion, however, also liberates benzoylacetone from its sodium compound. Sodium benzoylacetone is, however, also capable of adding benzoyl chloride:

$$
\text{III.}\quad
\begin{array}{c}
CH_3 \\
| \\
CONa \\
\| \\
CH.CO.C_6H_5
\end{array}
\;+\;
\begin{array}{c}
\\
Cl \\
| \\
CO.C_6H_5
\end{array}
\;=\;
\begin{array}{c}
CH_2 \\
| \\
C{<}^{ONa}_{Cl} \\
| \\
CH(CO.C_6H_5)_2,
\end{array}
$$
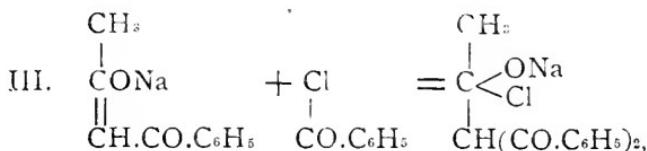
and the latter body, by again separating hydrochloric acid, leaves sodium dibenzoylacetone.

As sodium acetone has a structure represented by the formula $CH_3.CONa = CH_2$, it becomes highly probable that acetone is an unsaturated alcohol with the following composition: $CH_3—C.OH = CH_2$, and, in fact, many phases of the literature of this body, as well as some experiments which I am conducting in my laboratory, tend to show that such is really the case. I shall, however, defer this subject for a future communication after my present experimental work is completed, and shall also postpone until that time an extended discussion of my work on the action of chlorcarbonic ether, as well as of the action of carbon dioxide on acetone sodium.

In a former paper[1] I reported some experiments concerning the action of ethyl chlorcarbonate on acetone sodium. Further investigation has shown that the process is not at all as simple as the one which I then assumed to be the true one: several oils are formed which are extremely difficult to separate and which probably change their nature when distilled. By using phosphorus pentachloride as a reagent I have nearly succeeded in clearing up the investigation; a part of the work, however, is in need of further revision. In conclusion I wish to express my thanks to Messrs. D. M. Lichty and R. R. Putnam for their valuable assistance and active interest in carrying on this work.

August, 1893.

[1] This Journal **13**, 322.

REVIEWS.

DIE THERMODYNAMIK IN DER CHEMIE. Von J. J. VAN LAAR. Leipzig: W. Engelmann. (196 pp. Mark 7.)

The rapidly-growing interest of chemists in the problems and results of physical chemistry has created a need for a concise presentation of the thermodynamical theory of chemical processes, prefaced by an outline of the principles and methods of thermodynamics. This need the book by van Laar is intended to meet. In it are discussed successively the fundamental units; the first law; energy and entropy; van der Waals' theory of vapors (rather exhaustively); the $\delta \log K$ equilibrium-formulæ; and the recent theoretical work of Planck; together with varied applications in the theory of solutions of electrolytes. The treatment is of a decidedly mathematical character. J. E. T.

DIE LEHRE VON DER ELEKTRIZITAET. Von G. WIEDEMANN. IIte Auflage; Band I. Braunschweig: Vieweg. (1023 pp. Mark 26.)

The great extent of recent investigations in the subject of electricity has rendered necessary a new and rewritten edition of Wiedemann's monumental work. The first of its five volumes is now ready and the others are to follow in the near future. The book presents in organized form the results of all research-work in electricity up to the close of 1892, including a critical discussion of the material, and complete citations of the original papers— this making it invaluable as a reference-book in any branch of the subject. The present volume treats of the general properties of electricity, and the development of electricity in heterogeneous systems; including under the latter head all determinations of the conductivities of solutions, the corresponding experimental methods, the electromotive forces of different combinations, and a chapter on voltaic cells. J. E. T.

AMERICAN

CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LXXIX.—THE REACTIONS OF SODIC ALCOHOLATES WITH TRIBROMTRINITROBENZOL.[1]

Second Paper.

BY C. LORING JACKSON AND W. H. WARREN.

In our first paper on this subject we described some experiments which led to the replacement of nitro groups in symmetrical tribromtrinitrobenzol by ethoxy or methoxy radicles. These observations seemed to us of special interest because the three nitro groups are in the meta position in this compound, and, so far as we were aware, no case was known in which a nitro group in this position to others had been removed from the benzol ring. In fact the so-called rule of Laubenheimer stated that a nitro group is replaced only when it is in the ortho position to another. Even with the halogens, cases where a radicle in the meta position exercises a loosening effect on another are very rare, the only one which occurs to us being the conversion of symmetrical tribrombenzol into dibromanisol by the action of sodic methylate.[2]

Soon after the appearance of our paper C. A. Lobry de Bruyn published an account[3] of some experiments with symmetrical trinitrobenzol and sodic methylate from which he obtained dinitro-

anisol, thus again removing a nitro group in the meta position to others. At the same time, in an interesting discussion[1] of the replacement of nitro groups in aromatic compounds, he showed that Laubenheimer's rule must be abandoned, since para as well as ortho nitro compounds are attacked by alcoholates and other reageants with the removal of nitro groups. This publication brought to our notice an earlier paper[2] by him, in which he states that by the action of alcoholic potassic cyanide on metadinitrobenzol one nitro group is replaced by the ethoxy (or methoxy) radicle, but at the same time an atom of cyanogen is substituted for one atom of hydrogen, giving as the product $C_6H_3.NO_2.OC_2H_5.CN$. This curious result seems to have more affinity with the additions of hydrocyanic acid to nitrohalogen benzols studied by v. Richter[3] than to simple substitution; but nevertheless we have here the replacement of a meta nitro group by another radicle. As Lobry de Bruyn's later work was published almost simultaneously with ours (although a little later), and had grown out of his earlier researches, we felt that the study of substitutions of nitro groups in simple trinitro compounds should properly belong to him, and after a pleasant correspondence on the subject it has been agreed that he should follow out this line of work, while we confine ourselves, so far as the removal of nitro groups is concerned, to the completion of our study of tribromtrinitrobenzol.

At present, therefore, we know only three meta nitro compounds from which nitro groups have been removed: dinitrobenzol, symmetrical trinitrobenzol, and symmetrical tribromtrinitrobenzol.

Lobry de Bruyn's work shows that the removal of nitro groups observed by us is caused by the position of these nitro groups, but the presence of the three meta bromine atoms evidently also has a loosening effect on the nitro groups, as we have replaced two of these groups by ethoxy radicles, whereas in the trinitrobenzol only one was replaced.

In taking up the study of the subject again, we first examined the action of tribromtrinitrobenzol and sodic ethylate more carefully, to see whether the bromine atoms were not also affected by it, and found that in addition to the tribromnitroresorcin diethyl ether there is always formed a quantity of trinitrophloroglucin triethyl ether, $C_6(OC_2H_5)_3(NO_2)_3$, melting at 119°–120°; as, how-

[1] Recueil trav. chim. **9**, 210.   [2] *Ibid.* **2**, 205.
[3] Ber. d. chem. Ges. **4**, 465; **7**, 1145; **8**, 1418.

ever, this substance is easily decomposed by sodic hydrate, the amount of it obtained as such is small, unless special precautions are taken to exclude atmospheric moisture. When such precautions are not taken, the trinitrophloroglucin triethyl ether is converted into the diethyl ether $C_6OH(OC_2H_5)_2(NO_2)_3$, melting at 89°, or trinitrophloroglucin itself, $C_6(OH)_3(NO_2)_3$ (which melts at 167° instead of 158°, the point given by Benedikt,[1]), and these substances pass into the aqueous wash-waters as sodium salts. It follows therefore that the action of sodic ethylate on tribromtrinitrobenzol consists of the two following reactions, which take place parallel to each other:

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr.$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2.$$
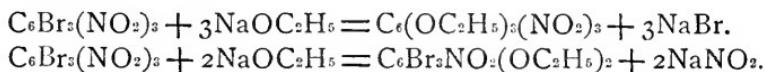
We observed further, that, if benzol and alcohol were used as the solvents instead of alcohol alone, more of the phloroglucin ether was obtained than when the solvent was only alcohol, and this led us to study the action quantitatively by determining the amounts of sodic nitrite and bromide formed, when we found that the amount of nitrite averaged with the benzol and alcohol 33.49 per cent.; with alcohol alone, 45.92 per cent. There was also a difference in the reverse direction with the sodic bromide, but the percentages of this obtained under parallel conditions varied so materially that no careful comparison was possible. The percentages of sodic nitrite removed were, on the other hand, remarkably constant. We have not succeeded in finding any satisfactory explanation for this effect of the presence of benzol in promoting the formation of the trinitrophloroglucin triethyl ether (produced by the first reaction), and diminishing the amount of tribromnitroresorcin diethyl ether formed by the second reaction given above.

We have also tried the action of several other alcoholates on tribromtrinitrobenzol, obtaining the following compounds: $C_6Br_3NO_2(OCH_3)_2$, melting at 126°; $C_6(OCH_3)_2OH(NO_2)_3$, melting at 77–78°; $C_6(OC_3H_7)_3(NO_2)_3$, from normal propyl alcohol, melting-point 109°–110°; the corresponding iso-compound melting at 130°; and $C_6(OCH_2C_6H_5)_3(NO_2)_3$, melting at 171°. A quantitative comparison of the amounts of sodic nitrite formed by different alcoholates indicated that the percentage removed dimin-

[1] Ber. d. chem. Ges. **11**, 1376.

ishes as the molecular weight of the alcohol increases, but there were several exceptions to this general rule.

We have also found that sodic ethylate decomposes the triphenyl ether of trinitrophloroglucin, converting it into the triethyl ether, while phenol is set free; and that sodic ethylate when heated with the tribromnitroresorcin diethyl ether removes from it two atoms of bromine which are replaced by hydrogen, so that the product is bromnitroresorcin diethyl ether, $C_6H_2BrNO_2(OC_2H_5)_2$, melting at $115°$;—an observation which will be of value in discovering the cause of the strange replacements of bromine by hydrogen so often found in the course of this work.

PART I.—ACTION OF SODIC ETHYLATE ON TRIBROMTRINITROBENZOL.

In our earlier paper[1] on this subject we showed that sodic ethylate brought about a replacement of two of the nitro groups in tribromtrinitrobenzol by two ethoxy radicles forming tribromnitroresorcin diethyl ether, $C_6Br_3NO_2(OC_2H_5)_2$, as the principal product if alcohol was used as the only solvent and the mixture carefully cooled. There remained, however, several points which needed more careful examination, especially the effect upon the reaction of differences of temperature, the effect of using different solvents, and the source of the sodic bromide which was always formed in addition to the sodic nitrite. The results of our work on these subjects are given in the following paragraphs.

The experiments described in our first paper had led us to think that the tribromnitroresorcin diethyl ether was formed only when the mixture of tribromtrinitrobenzol and sodic ethylate was carefully cooled. To test the accuracy of this conclusion, we dissolved some tribromtrinitrobenzol in alcohol and a little benzol with the aid of heat, and added to the boiling solution, in small quantities at a time, enough sodic ethylate to give three molecules of the ethylate to each molecule of tribromtrinitrobenzol. As soon as all the ethylate had been added, the bright scarlet solution was allowed to cool, and then evaporated spontaneously. The aqueous washings of the residue gave a strong test for a nitrite, and also for a bromide. The portion insoluble in water was purified by crystallization from alcohol until it showed a melting-point of $100°$

[1] This Journal **13**, 184.

(the tribromnitroresorcin diethyl ether melts at 101°), when it was analyzed with the following result:

0.2076 gram substance gave by Carius' method 0.2601 gram AgBr.

	Calculated for $C_6Br_3NO_2(OC_2H_5)_2$.	Found.
Bromine	53.57	53.32

This analysis, with the melting-point, leaves no doubt that the substance is the expected tribromnitroresorcin diethyl ether, and therefore that the temperature of the reaction does not affect the nature of the principal product. We have accordingly omitted the cooling in our subsequent preparations of this body, simply allowing the mixture of tribromtrinitrobenzol, sodic ethylate, and alcohol to stand over night at ordinary temperatures.

The Modification of the Action when Benzol is used as one of the Solvents.

To study this subject the following experiment was tried: 10 grams of tribromtrinitrobenzol were dissolved in dry benzol and an alcoholic solution of the sodic ethylate from 1.5 grams of sodium added (these proportions are essentially three atoms of sodium to each molecule of tribromtrinitrobenzol). The first drop of the solution of sodic ethylate turned red as it was added, the color fading to yellow as the drop mixed with the liquid, so that, after all the ethylate had been added, the liquid had assumed an orange-red color. No evolution of heat was observed during the reaction. To make sure that the action was complete, the mixture was allowed to stand over night in a corked flask at ordinary temperatures, and was then allowed to evaporate spontaneously, after which the residue was washed with water to remove the soluble salts.

Substances insoluble in Water.—The residue after washing with water was crystallized repeatedly from alcohol, and in this way a considerable quantity of the tribromnitroresorcin diethyl ether melting at 101° was obtained from the first crystals, while the mother-liquors yielded a smaller quantity of another substance which when pure melted at 119°–120°. This was dried at 100°, and analyzed with the following results:

I. 0.2159 gram substance gave 0.3284 gram CO_2 and 0.0914 gram H_2O.

II. 0.2080 gram substance gave 22.5 cc. N at 21° and 759.3 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.	
		I.	II.
Carbon	41.75	41.49	...
Hydrogen	4.35	4.70	...
Nitrogen	12.17	...	12.30

It contained no bromine. There can be no doubt, therefore, that the product was the triethyl ether of trinitrophloroglucin, and that the formation of this substance produced the sodic bromide which was always obtained by the action of sodic ethylate on tribromtrinitrobenzol.

Properties of Trinitrophloroglucin Triethyl Ether.—This substance crystallizes in long slender plates, terminated usually by one plane at a very sharp angle to the sides. These crystals are often united longitudinally into broader plates, which frequently have serrated ends, and may reach more than a centimeter in length and a millimeter in breadth. The color is white, but it turns brownish on exposure to the air. It melts at 119°–120°; is soluble in cold ethyl or methyl alcohol, freely soluble in either of these solvents when hot; very freely soluble in benzol, chloroform, or acetone; freely soluble in glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroïn; essentially insoluble in water, whether cold or hot. The three strong acids have no perceptible action on it, hot or cold, except that it is dissolved by hot strong nitric acid, but on dilution it is precipitated unchanged, to judge by the melting-point. We have tried no experiments on its saponification by the long-continued action of acids. A cold aqueous solution of sodic hydrate had no action upon it, and only a slight action when heated, but in alcoholic solution sodic hydrate decomposes it even in the cold, more rapidly when hot, forming a reddish-yellow solution of the sodium salt of a phenol.

In addition to the tribromnitroresorcin diethyl ether and trinitrophloroglucin triethyl ether, we have always obtained from the crystallization a considerable amount of a substance which accumulated in the mother-liquors and separated from its alcoholic solution as an oil solidifying after standing for some weeks. We have devoted a great deal of time to the study of this substance, because it appeared in such quantity that we thought it must be a principal product of our reaction; but this work has shown that it consists principally of the products already described, mixed with very little of an oily substance which prevents them from crystallizing as usual. In a preparation from 30 grams of tribrom-

trinitrobenzol, the mother-liquors gave 4.3 grams of the more-or-less liquid fraction, but this amount was reduced to 1.2 grams after removing the trinitrophloroglucin triethyl ether completely by treatment with alcoholic sodic hydrate, and the tribromnitroresorcin diethyl ether as nearly as possible by crystallization from alcohol of the mixture solidified by standing for several months. All our attempts to free the oily product completely from the tribromnitroresorcin diethyl ether have failed, so that we are unable to give any account of its composition.

Products soluble in Water.—In purifying the products of the action of sodic ethylate upon tribromtrinitrobenzol, the aqueous solution formed by washing the residue from spontaneous evaporation contained a large amount of organic matter, as was indicated by its orange-red color. In order to determine its nature, the solution was acidified with dilute sulphuric acid, which gave a precipitate, but did not remove all the organic matter present, since the filtrate still showed a strong yellow color. This precipitate was washed with water, in which it is nearly insoluble, until the washings ceased to show a yellow color, and then purified by converting it into its sodium salt, filtering the solution, reprecipitating with dilute sulphuric acid, and finally crystallizing from dilute alcohol until it showed the constant melting-point 89°, when it was dried *in vacuo* and analyzed with the following results:

0.2285 gram substance gave 0.3145 gram CO_2 and 0.0817 gram H_2O.

	Calculated for $C_6(OC_2H_5)_2OH(NO_2)_3$.	Found.
Carbon	37.85	37.53
Hydrogen	3.47	3.97

To confirm these results, a portion of the substance was treated with an aqueous solution of less than the calculated amount of sodic hydrate necessary to convert it into the sodium salt; the solution of the salt was filtered from the unaltered phenol, the filtrate evaporated to dryness, and the residue washed with benzol to remove any traces of the free phenol which might have dissolved in the water. It was then dried at 100°, and the sodium salt thus obtained analyzed with the following results:

I. 0.1498 gram substance yielded 0.0329 gram Na_2SO_4.

II. 0.2410 gram salt gave 0.0524 gram Na_2SO_4.

	Calculated for $C_6(OC_2H_5)_2ONa(NO_2)_3$.	Found. I.	II.
Sodium	6.78	7.11	7.04

These analyses leave no doubt that the substance is the diethyl ether of trinitrophloroglucin. As it has not been described heretofore, we add its properties.

Properties of the Diethyl Ether of Trinitrophloroglucin.—This substance crystallizes in square-ended, rather short prisms, or in longer flat needles, also, usually, with square ends, although sometimes instead of this they are very sharp; both forms are frequently arranged in fan-like groups. It has a straw-yellow color, and melts at 89°. Very freely soluble in ethyl or methyl alcohol, ether, benzol, glacial acetic acid, chloroform, or acetone; soluble in carbonic disulphide; very slightly soluble in ligroïn; slightly soluble in cold water, more soluble in hot; dilute alcohol is the best solvent for it. The three strong acids have no apparent action on it, hot or cold. Sodic hydrate dissolves it, forming an orange-red sodium salt, which crystallizes in fine needles. Ammonic hydrate dissolves it rather slowly, forming a yellow solution. Solutions of sodic or acid sodic carbonate also dissolve it with evolution of carbonic dioxide, forming yellow solutions; it is evident, therefore, that the substance possesses strongly acid properties.

The filtrate from the diethyl ether of trinitrophloroglucin, which had changed from red to yellow on acidification, after concentration on the water-bath deposited upon cooling rather ragged, thick yellow needles; but if the evaporation was carried on spontaneously, yellow hexagonal prisms were obtained, which dissolved in alkalies more easily than in water, and gave, according to the amount of alkali used, red or yellow salts, crystallizing in hair-like needles—properties which indicated that the substance was a polyatomic nitrophenol, probably the trinitrophloroglucin. This substance has been described by Benedikt[1] as crystallizing from water in hexagonal prisms, and melting at 158°; we accordingly purified our substance by crystallization from water, but found that it melted as high as 167°. In spite of the want of agreement between this melting-point and that given by Benedikt, the crystalline form and other properties indicated that the substance was trinitrophloroglucin, and this was proved to be the case

[1] Ber. d. chem. Ges. **11**, 1376.

by the following analyses. As Benedikt found that trinitrophloroglucin contains one molecule of water of crystallization, we examined our substance for this:

I. 0.7721 gram air-dried substance heated to 105° lost 0.0477 gram.

	Calculated for $C_6(OH)_3(NO_2)_3H_2O$.	Found. I.
Wate	6.45	6.18

The air-dried substance lost 0.0015 gram at 56°, and showed a tendency to sublime at 105°.

II. 0.2126 gram compound, dried at 105°, gave 0.2105 gram CO_2 and 0.0304 gram H_2O.

III. 0.2260 gram compound, dried at 105°, gave 31.2 cc. N at 17° and 775.8 mm.

	Calculated for $C_6(OH)_3(NO_2)_3$.	Found. II.	III.
Carbon	27.58	27.01[1]	...
Hydrogen	1.15	1.59	...
Nitrogen	16.09	...	16.37

It is evident from these analyses that the substance is *trinitrophloroglucin*, and therefore it becomes important to explain the very marked difference between the melting-points observed by Benedikt and by us. We are inclined to ascribe this to the water of crystallization, as the melting-point 167° was obtained with the substance dried at 105° and used for analysis, whereas with samples which had been only air-dried (or dried at 50°) we obtained melting-points as low as 160°–161°, that is, only 2° or 3° above the 158° obtained by Benedikt.

In order to determine whether the formation of the trinitrophloroglucin and its diethyl ether was due to a direct reaction, or to the secondary reaction on the trinitrophloroglucin triethyl ether of some sodic hydrate formed by the moisture of the air acting on the sodic ethylate, the following experiment was tried: Absolute alcohol made in the usual way with quicklime was treated with a small quantity of sodium, and then the unaltered alcohol distilled off from the sodic alcoholate in a perfectly dry apparatus, which communicated with the outer air only through a drying-tube; to the distillate in the flask which served as a

[1] The percentages of carbon and hydrogen are as near to those required by the formula as could be expected when the difficulty of making a combustion of this explosive substance is considered.

receiver, a quantity of bright sodium was added as quickly as possible, after which it was closed at once with a cork carrying a drying-tube. When the reaction was at an end, and the solution of sodic ethylate had cooled, 5 grams of dry tribromtrinitrobenzol were added, and the mixture allowed to stand over night closed with the cork carring the drying-tube. The solution, which had turned red, was acidified with dilute sulphuric acid and allowed to evaporate spontaneously, when after purification it yielded 2 grams of the triethyl ether of trinitrophloroglucin instead of 0.12 gram, the usual yield when no special precautions were taken to exclude atmospheric moisture. It is evident, therefore, that the trinitrophloroglucin triethyl ether is formed at first, and afterward saponified wholly or in part by sodic hydrate produced by the action of moisture on the sodic ethylate. That most of this sodic hydrate is formed during the spontaneous evaporation of the alkaline solution was shown by two experiments, in which the ethyl ether of trinitrophloroglucin was treated with a solution of sodic ethylate, with all the precautions described above, except that in one of these experiments the alkaline liquid was allowed to evaporate spontaneously, when all the triethyl ether was saponified, the whole product being soluble in water, whereas in the other, which was acidified before evaporating, 0.65 gram of unaltered triethyl ether was recovered, 0.7 gram having been the amount used.

Lobry de Bruyn[1] has encountered similar difficulties in studying the action of sodic ethylate upon the unsymmetrical trinitrobenzol (1, 2, 4), as in this case considerable quantities of dinitrophenol were obtained, whereas with sodic methylate the dinitroanisol was the only organic product.

Experiments with Acetic Ester as the Solvent.

After we had found that the presence of benzol diminished the tendency of sodic ethylate to replace nitro groups in the tribromtrinitrobenzol, we tried some experiments on the action of other solvents. The choice here, however, was limited, because there are so few liquids belonging to a different class from benzol which have any considerable solvent action on the tribromtrinitrobenzol; in fact, acetone and acetic ester were the only ones easily obtained which fulfilled this condition, and acetone had to be rejected, as

[1] Recueil trav. chim. **9**, 191.

it seemed to take part in the reaction, giving a dark brownish red solution, very different from the orange-red obtained in all other cases. This result was not unexpected after the work of Freer[1] (published only in the preliminary paper at the time we tried this experiment), and since we did this work we have seen the paper of Janovsky,[2] describing the colors which he obtained by the action of acetone and potassic hydrate on dinitro compounds of the aromatic series.

In our first experiment with acetic ester we used the commercial article without especially drying it. The action was carried on in the usual way, 5 grams of tribromtrinitrobenzol being used. The aqueous washings gave tests for nitrite and bromide, but the organic product was found to consist principally of the tribromdinitrophenetol melting at 147°, described in our previous paper.[3] For greater certainty it was analyzed, with the following results:

I. 0.2972 gram substance gave by Carius' method 0.3721 gram AgBr.

II. 0.2788 gram substance gave 0.3535 gram AgBr.

	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$.	Found. I.	II.
Bromine	53.46	53.27	53.96

This experiment called our attention to a subject which we had already studied without any very definite result, that is, the conditions under which the phenetol $C_6Br_2(NO_2)_2OC_2H_5$ is formed, rather than the tribromnitroresorcin diethyl ether, $C_6Br_3NO_2(OC_2H_5)_2$. Our previous work had led us to the conclusion that the presence of a trace of water is favorable to the formation of the phenetol, as on one occasion when benzol not dried over sodium was used this substance was obtained, and in the experiment described in our previous paper, which yielded a quantity of the phenetol, common benzol was also used, whereas in all the preparations made by us with absolute benzol and alcohol not a trace of the phenetol has been found. On the other hand, in a repetition of the experiment with common benzol, and in one in which undried benzol and common, instead of absolute, alcohol were used, only the resorcin ether $C_6Br_3NO_2(OC_2H_5)_2$ was isolated. To test this question still further, we repeated the experiment described at the beginning of this section, using carefully dried acetic ester instead of the com-

[1] This Journal **12**, 355; **13**, 308; Freer and Higley: **13**, 322.
[2] Ber. d. chem. Ges. **24**, 971.   [3] This Journal **13**, 187.

mercial article, and obtained decidedly less of the phenetol with a large proportion of the tribromnitroresorcin diethyl ether, thus confirming, although not absolutely proving, our previous inference that the presence of a trace of moisture is favorable to the formation of the phenetol.

Action when Alcohol is the only Solvent used.

This action has been already described in our first paper, but after we had found, as described in the preceding sections, that the action when benzol was present took place in the two parallel reactions,

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr, \text{ and}$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2,$$
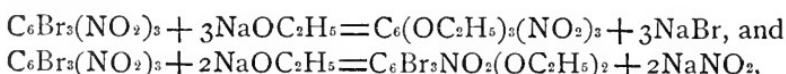
it became of interest to determine whether the first of these reactions took place if alcohol was the only solvent, or whether the action consisted of the second alone, as we had supposed when we published our first paper. A very little work was sufficient to prove the presence of the trinitrophloroglucin triethyl ether, or the phenols formed by its saponification, among the products of the reaction when alcohol was the only solvent, thus showing that the action in the two cases is parallel, although the first reaction takes place to a much more limited extent when alcohol is the only solvent, than when a mixture of alcohol and benzol is used. Our attempts to determine the relative amounts of the products of each of these two reactions are described in a later section.

Preparation of Tribromnitroresorcin Diethyl Ether and Trinitrophloroglucin Triethyl Ether.

It follows from what has been said in the preceding sections, that the best way to prepare tribromnitroresorcin diethyl ether is to allow tribromtrinitrobenzol (10 parts) to stand in the cold for twelve hours with an alcoholic solution of sodic ethylate (from 1.5 parts of sodium), then, after the solvent has evaporated spontaneously, to wash the residue with water, and after one crystallization of the insoluble part from alcohol, treat it in the cold with an alcoholic solution of sodic hydrate for about twelve hours to saponify the trinitrophloroglucin triethyl ether also present. The sodium salt thus formed is washed out, and the residue crystallized from alcohol until it shows the melting-point of 101°.

If, on the other hand, trinitrophloroglucin triethyl ether is to be prepared, the tribromtrinitrobenzol should be dissolved in anhydrous benzol (dried with sodium) and the alcoholic solution of sodic ethylate added to this solution. Every precaution should be taken to exclude even traces of moisture, and after the twelve hours standing the solution should be acidified with dilute sulphuric acid before allowing it to evaporate spontaneously. The residue, after washing with water, is purified by crystallization from alcohol, which separates the two ethers formed by the parallel reactions.

Quantitative Study of the Action of Sodic Ethylate on Tribromtrinitrobenzol.

After we had proved that this action takes place in these two different ways,

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr, \text{ and}$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2,$$
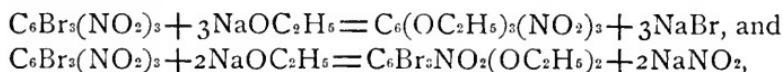
it became of interest to determine the relative extent of each of the parallel reactions under varying conditions, and the easiest way to do this was obviously to find the amount of sodic bromide and sodic nitrite formed, as the first must have proceeded from the reaction giving the trinitrophloroglucin triethyl ether, the second from that producing the tribromnitroresorcin diethyl ether. In addition to this we have weighed the amount of organic matter formed, and have made some not very successful attempts to determine the amount of its several constituents. The method adopted was the following: A weighed quantity of tribromtrinitrobenzol mixed with the solvent and the ethylate in the proportion of three atoms of sodium to each molecule, stood over night in a corked flask. The liquid was then allowed to evaporate spontaneously, and the residue washed thoroughly with water. The weight of the organic matter insoluble in water was taken, and also that of the aqueous solution which contained all the sodium salts; this was then divided into weighed parts, one of which was acidified with nitric acid, and after filtering out and weighing the diethyl ether of trinitrophloroglucin the amount of sodic bromide it contained was determined with argentic nitrate. The second portion of the aqueous liquid was used for the determination of the amount of sodic nitrite, but it was not easy to find a method which would

be applicable in this case. The common way of determining a nitrite with potassic permanganate was inadmissible, because of the presence of organic matter. The urea-method in its usual form was also inapplicable because of the presence of sodic carbonate, but finally by modifying it in the following way we succeeded in obtaining satisfactory results : The weighed portion of the solution to be tested, mixed with a sufficient quantity of urea, was poured into a little flask, and a small test-tube containing dilute sulphuric acid put into the flask supported in a vertical position by a piece of platinum wire projecting from its upper end and resting against the neck of the flask. The apparatus was then filled with carbonic dioxide from a heated tube containing magnesite, after which by shaking the flask the sulphuric acid was added to its contents in small quantities at a time, and the nitrogen given off collected over a solution of potassic hydrate, and measured in the usual way. It is necessary to heat the flask gently toward the end of the operation to drive off all the nitrogen. One-half of the nitrogen collected is derived from the sodic nitrite. To test the accuracy of the method two determinations of the nitrogen in commercial sodic nitrite were made by it, which gave,—

	Found.	
Nitrogen	18.09	18.11

and as they agreed with each other, and came tolerably near to the usual percentage of nitrogen in commercial sodic nitrite (between 19 and 20 per cent.), it was evident that the method was accurate enough for our purposes. A third portion of the aqueous liquid was in two experiments used for the determination of the trinitrophloroglucin, but we give our results with a great deal of hesitation, as we were unable to find any satisfactory quantitative method ; methods based upon extraction with an organic solvent, or the precipitation of the barium salt, which Benedikt says is insoluble, led to no result. We were therefore driven to determining the amount of nitrogen in the residue obtained by evaporating to dryness a portion of the aqueous solution acidified with sulphuric acid, and calculating from this the amount of trinitrophloroglucin, on the assumption, which at best can be but approximately correct, that this was the only substance containing nitrogen left in the residue.

Experiments in which Alcohol was the only Solvent used.—I. Weight taken, 10.556 grams. Weight of aqueous solution, 135.4

grams; 8.6 grams solution gave 16.9 cc. N from the NaNO$_2$ at 23° and 763.8 mm.; 28.2 grams solution gave 1.1718 grams AgBr; 20.8 grams solution gave, after the nitrous acid had been expelled by sulphuric acid, 8.2 cc. N at 23° and 767.8 mm.: 54 4 grams solution gave 0.808 gram diethyl ether of trinitrophloroglucin. Organic matter insoluble in water$=6.97$ grams.

II. Weight taken, 10.1582 grams. Weight of aqueous solution, 164.55 grams; 15.95 grams solution gave 24.65 cc. N from NaNO$_2$ at 26.5° and 765 mm.; 58.45 grams solution gave 1.6583 grams AgBr, and yielded 0.8499 gram of the diethyl ether of trinitrophloroglucin. Organic matter insoluble in water$=5.78$ grams.

III. Weight taken, 1.0366 grams. Weight of aqueous solution, 121.4 grams; 62.5 grams solution gave 13.6 cc. N from NaNO$_2$ at 21° and 765.2 mm.; 58.9 grams solution gave 0.2700 gram AgBr. Organic matter insoluble in water $=0.48$ gram.

IV. Weight taken, 10 grams.[1] Weight of aqueous solution, 142.9 grams; 13.7 grams solution gave 25.7 cc. N from NaNO$_2$ at 29.5° and 759.2 mm.; 55.1 grams solution gave 1.9029 grams AgBr. 1.7 grams diethyl ether of trinitrophloroglucin were obtained from 10 grams used. Weight of organic matter insoluble in water $=6.4$ grams.

V. Weight taken, 10 grams.[1] Weight of aqueous solution, 114.8 grams; 14.6 grams solution gave 32.3 cc. N from NaNO$_2$ at 28° and 764.1 mm.; 48.7 grams solution gave 0.9573 gram AgBr; 2.4 grams diethyl ether of trinitrophloroglucin were obtained from 10 grams used. Weight of organic matter insoluble in water $=5.6$ grams.

The results of these experiments are given in tabular form at the end of the next section.

Experiments in which Benzol was the Principal Solvent used.— VI. Weight taken, 10.0220 grams. Weight of aqueous solution, 126.65 grams; 11.7 grams solution gave 17.15 cc. N from NaNO$_2$ at 24° and 764.5 mm.; 28.7 grams solution gave 1.6952 grams AgBr; 24.7 grams solution gave, after the nitrous acid had been expelled by sulphuric acid, 12.2 cc. N at 25° and 766.1 mm. Acid precipitated from these 24.7 grams solution 0.3374 gram diethyl ether of trinitrophloroglucin. Organic matter insoluble in water $=4.99$ grams.

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[1] This weight is accurate only to tenths of a gram.

VII. Weight taken, 10.1976 grams. Weight of aqueous solution, 135.2 grams; 19.3 grams solution gave 27.2 cc. N from $NaNO_2$ at 25° and 750.9 mm.; 43.9 grams solution gave 1.6158 grams AgBr; 72 grams solution gave 1.4724 grams diethyl ether of trinitrophloroglucin. Organic matter insoluble in water $= 5.51$ grams.

VIII. Weight taken, 1.2524 grams. Weight of aqueous solution, 37.3 grams; 24.2 grams solution gave 14.3 cc. N from $NaNO_2$ at 19° and 771.5 mm.; 13.1 grams solution gave 0.4097 gram AgBr. Organic matter insoluble in water $= 0.55$ gram.

IX. Weight taken, 1.2682 grams. Weight of aqueous solution, 38.1 grams; 19.7 grams solution gave 12 cc. N from $NaNO_2$ at 24° and 767.3 mm.; 18.4 grams solution gave 0.5082 gram AgBr. Organic matter insoluble in water $= 0.58$ gram.

X. Weight taken, 1.2287 grams. Weight of aqueous solution, 53 65 grams; 17.65 grams solution gave 7.7 cc. N from $NaNO_2$ at 25° and 766.1 mm.; 18.9 grams solution gave 0.2664 gram AgBr and 0.0854 gram diethyl ether of trinitrophloroglucin. Organic matter insoluble in water $= 0.68$ gram.

In the following tables the first column gives the number of the experiment, and the weight of tribromtrinitrobenzol used; the second, the percentage of nitrogen removed as sodic nitrite referred to the total amount of nitrogen which could be removed from the tribromtrinitrobenzol by this reaction, that is, two out of the three atoms of nitrogen, because the product $C_6Br_3NO_2(OC_2H_5)_2$ contains one nitro group; the third column gives the percentage of the total bromine removed as sodic bromide; the fourth, the weight of the organic matter insoluble in water; the fifth, the weight of the diethyl ether of trinitrophloroglucin; and the sixth, the weight of trinitrophloroglucin calculated from the volume of nitrogen obtained from the residue after acidification with sulphuric acid.

TABLE I.—*Action of Sodic Ethylate in Ethyl Alcohol.*

	Weight of $C_6Br_3(NO_2)_3$ used.	Percentage of Nitrogen.	Percentage of Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH$ $(NO_2)_3$.	Weight of $C_6(OH)_3$ $(NO_2)_3$.
I.	10.556	45.88	42.53	6.97	2.0	0.38
II.	10.1582	44.85	36.67	5.78	2.39	...
III.	1.0366	46.95	42.85	0.48	...	...
IV.	10.	46.86	39.39	6.4	1.7	...
V.	10.	45.06	18.02	5.6	2.4	...

TABLE II.—*Action of Sodic Ethylate with Benzol and Alcohol.*

	Weight of $C_6Br_3(NO_2)_3$.	Nitrogen.	Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2$ $OH(NO_2)_3$.	Weight of $C_6(OH)_3(NO_2)_3$.
VI.	10.022	33.58	59.54	4.99	1.73	0.44
VII.	10.1976	33.09	38.91	5.51	2.8	...
VIII.	1.2524	33.03	74.32	0.55	...	...
IX.	1.2682	33.31	66.21	0.58	...	...
X.	1.2287	34.42	49.10	0.68	...	...

An examination of these tables shows that the percentages of nitrogen removed are fairly constant under each set of conditions, the maximum differences being, in Table I, 2.1 per cent., in Table II, 1.39 per cent.,—which are surprisingly small when the nature of the process and the roughness of the manipulations are considered. These numbers, therefore, are well fitted to give an idea of the effect on the reactions of the presence of benzol, and they show that it diminishes the amount of sodic nitrite formed, since the percentage of nitrogen removed when alcohol alone is present, averages 45.92 (maximum 46.95, minimum 44.85), whereas if the solvent is partly benzol the average percentage falls to 33.49 (maximum 34.42, minimum 33.03).

On the other hand, no agreement is found in the amounts of bromine removed as sodic bromide, the maximum difference in Table I being 24.83 per cent., in Table II 35.41 per cent.; but in spite of this these results show that the presence of benzol favors the removal of bromine, since of the five determinations of bromine in presence of benzol (Table II), only one (38.91 per cent.) is below the largest percentage of bromine obtained (42.85 per cent.) when alcohol was the only solvent (Table I), and most of those in Table II are very far above those in Table I.

As to the numerical relations between the percentages of inorganic compounds formed under the two sets of conditions, it is to be observed that in the alcohol series the amounts of nitrite and bromide are approximately equal. In the benzol series the amount of nitrite is almost exactly one-third of the total amount which could have been formed, and is in some cases about one-half that of the bromide. In most cases, between 80 and 90 per cent. of the tribromtrinitrobenzol used is accounted for by the amounts of inorganic salts formed. The experimental work is not accurate enough to allow a more careful discussion of this part of the sub-

ject, as not enough attention was paid to various details, such, for instance, as maintaining a constant temperature, and measuring accurately the amounts of solvent used.

In all the experiments with benzol given in Table II free alcohol was also present. To determine what influence this had on the reaction, we made another experiment, in which all free alcohol was carefully excluded, so that in this case benzol was the only liquid present.

XI. Weight taken, 5.0453 grams. Weight of aqueous solution, 83.4 grams; 19.6 grams solution gave 23.8 cc. N at 28.5° and 760.1 mm.; 43.4 grams solution gave 1.9610 grams AgBr and 1.55 grams of the diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 2.75 grams.

From these results 35.34 per cent. of nitrogen and 59.62 per cent. of bromine are obtained. The percentage of nitrogen, when benzol and alcohol were used as the solvents, averaged 33 49, so that this experiment shows that the presence of alcohol does not materially affect the result. The somewhat high percentage of nitrogen in this experiment may be due to the fact that the mixture stood two days instead of the usual twelve hours. This subject of the effect of time on the action will be discussed later in the paper.

We have also made two quantitative determinations, in which acetic ester was used with a little alcohol as the solvent.

XII. Weight taken, 1.0412 grams. Weight of aqueous solution, 58 grams; 17.5 grams solution gave 0.63 cc. N at 23.5° and 758.9 mm.; 40.5 grams solution gave 0.4504 gram AgBr.

XIII. Weight taken, 1.0271 grams. Weight of aqueous solution, 49.1 grams; 18 grams solution gave 2.8 cc. N at 22.5° and 760.8 mm.; 31.1 grams solution gave 0.4902 gram AgBr.

		Nitrogen.	Bromine.
XII.	1.0412	3.62	50.06
XIII.	1.0271	13.49	60.15

We are inclined to regard No. XII with suspicion; but No. XIII alone shows that acetic ester has an even more unfavorable influence than benzol on the formation of the sodic nitrite; this is probably due to the fact that in this case there is a tendency to form the tribromdinitrophenetol, which would yield half as much sodic nitrite as the tribrommononitroresorcin diethyl ether formed when benzol was used.

Relative Yields of the Organic Products.—After we had determined the amounts of sodic bromide and nitrite formed by the two parallel reactions,

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr, \text{ and}$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2,$$
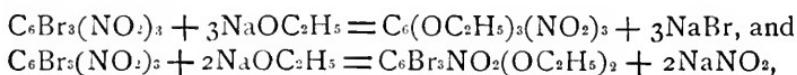
we tried to get an idea of the relative yields of the organic products. This could be done with some approach to accuracy in the case of the reaction which produces sodic bromide, because during the work most of the trinitrophloroglucin triethyl ether was converted into the salts of trinitrophloroglucin or its diethyl ether, both of which can be easily separated from the other organic products on account of their solubility in water. With the tribromnitroresorcin diethyl ether, on the other hand, no such approach to accuracy was obtained, because it could be purified only by crystallization, and a large portion of it remained mixed with the viscous impurity already mentioned. To obtain the following results, the organic matter insoluble in water, obtained from two experiments, was repeatedly crystallized from alcohol, until as much pure tribromnitroresorcin diethyl ether and trinitrophloroglucin triethyl ether had been obtained as possible. To the amount of the latter, which was very small, were added the calculated amounts of the triethyl ether corresponding to the quantities found of free trinitrophloroglucin and its diethyl ether. Two pairs of experiments were studied in this way, one from the series in which alcohol was the only solvent, and one from that in which benzol was used.

Experiments I and II.—Alcohol the only solvent. 20.71 grams tribromtrinitrobenzol gave 12.75 grams organic matter insoluble in water, from which were obtained 5.11 grams $C_6Br_3NO_2(OC_2H_5)_2$, 1.4 grams same slightly impure, 5.1 grams semi-liquid fraction from the mother-liquor, and 0.49 gram $C_6(OC_2H_5)_3(NO_2)_3$. From the aqueous solution 4.39 grams $C_6OH(OC_2H_5)_2(NO_2)_3$ were obtained, corresponding to 4.77 grams triethyl ether, and 0.78 gram[1] $C_6(OH)_3(NO_2)_3$, corresponding to 1.03 grams triethyl ether, making the total yield of triethyl ether 6.29 grams.

Experiments VI and VII.—Benzol present. 20.21 grams tribromtrinitrobenzol gave 10.50 grams organic matter insoluble in

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[1] These numbers are only estimates, as the amounts of trinitrophloroglucin were determined only in Nos. I and VI, the weight found being doubled to give the numbers. It is to be remembered also that our method for determining the trinitrophloroglucin was far from satisfactory.

water, from which were obtained 3.25 grams $C_6Br_3NO_2(OC_2H_5)_2$, 1.36 grams $C_6(OC_2H_5)_3(NO_2)_3$, and somewhat less than 6 grams semi-liquid fraction from mother-liquors. From aqueous solution were obtained 4.53 grams $C_6OH(OC_2H_5)_2(NO_2)_3$, corresponding to 4.93 grams triethyl ether, and 0.88 gram[1] $C_6(OH)_3(NO_2)_3$, corresponding to 1.16 grams triethyl ether, making total yield triethyl ether 7.45 grams.

These results confirm the inference drawn from the percentage of sodic nitrite and bromide, that the presence of benzol is unfavorable to the reaction by which sodic nitrite is formed, but promotes that which yields sodic bromide; a fact which is shown more plainly by this collection of the results in tabular form:

	$C_6(OC_2H_5)_3(NO_2)_3$.	$C_6Br_3NO_2(OC_2H_5)_2$.
Alcohol alone (I and II)	6.29 grams.	5.11[1]
Benzol and alcohol (VI and VII)	7.45	3.25[1]

All our results, therefore, show that the presence of benzol is favorable to the elimination of bromine, unfavorable to that of nitro groups. The most probable theoretical explanation of this observation which has occurred to us depends on the effect of the change of solvents upon the amounts of the salts precipitated, but any discussion of this theory at present would not be worth while, because the principle on which it rests has not been tested by experiment, so far as we can find.

We have not succeeded in finding the cause of the very marked variations in the amounts of sodic bromide shown in Tables I and II. At first we feared they might be due to defects in our experimental work, but that this is not the case is shown by the following comparison of the weights of trinitrophloroglucin triethyl ether actually found with the amounts of this substance calculated from the percentages of bromine eliminated as sodic bromide in the same experiment. We have selected this body for the comparison because, as has been already stated, these weights were determined with a fair degree of accuracy.

	Calculated.	Found.
Alcohol alone (I and II)	6.30	6.29
Alcohol and benzol (VI and VII)	7.62	7.45

The agreement is much closer than we had any right to expect, and shows that the differences in the percentages of bromine are

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[1] These numbers are only approximations to the true yields.

due to absolute variations in the extent of the reaction by which the bromine is removed, since experiments VI and VII differ in this respect very widely (VI 59.54 per cent. of bromine, VII 38.91 per cent. of bromine); and yet the amount of the trinitrophloroglucin triethyl ether calculated from these different percentages of bromine corresponds almost exactly to that obtained experimentally.

Part II.—Action of other Alcoholates on Tribromtrinitrobenzol.

In addition to the work with sodic ethylate just described, we have tried the action of the sodium compounds of other alcohols on the tribromtrinitrobenzol, and give in the first place descriptions of the new compounds thus obtained, followed by a series of quantitative experiments similar to those tried with the ethylate.

Sodic Methylate.

The organic compound insoluble in water obtained by the action of sodic methylate on tribromtrinitrobenzol consisted in every experiment we have tried of the tribromnitroresorcin dimethyl ether, melting at 126°, and already described in our first paper;[1] as, however, we found that a considerable amount of sodic bromide was formed in these experiments, we turned our attention to the aqueous washings of this organic matter, in which it was evident that the product formed by the removal of the bromine was to be sought. Upon acidifying this aqueous solution with dilute sulphuric acid, a copious precipitate was obtained, which was only slightly soluble in water, and was purified by crystallization with the following precautions. The substance was dissolved in as small a quantity as possible of cold alcohol, water was then added until it began to grow turbid, when the solution was cleared by the addition of a drop or two of alcohol, and allowed to evaporate spontaneously, all these operations being carried on in the cold. When it showed the constant melting-point 77°–78°, it was dried and analyzed with the following results:

0.2298 gram substance gave 0.2792 gram CO_2 and 0.0597 gram H_2O.

	Calculated for $C_6(OCH_3)_2OH(NO_2)_3$.	Found.
Carbon	33.22	33.13
Hydrogen	2.42	2.89

[1] This Journal **13**, 188.

To confirm this result the sodium salt was made and analyzed; for this purpose 1 gram of the substance was treated with 0.1 gram of sodic hydrate dissolved in a little water, that is, decidedly less sodic hydrate than would be needed to convert the whole of the substance into its salt. The yellow solution thus obtained was evaporated to dryness at 100°, washed with benzol to remove the small quantity of the free phenol which had dissolved in the water, dried at 100°, and analyzed with the following result:

0.3730 gram salt gave 0.0874 gram Na_2SO_4.

	Calculated for $C_6(OCH_3)_2ONa(NO_2)_3$.	Found.
Sodium	7.39	7.59

These analyses and the analogy with the corresponding ethyl compound leave no doubt that the substance is the dimethyl ether of trinitrophloroglucin.

Properties of the Dimethyl Ether of Trinitrophloroglucin, $C_6(OCH_3)_2OH(NO_2)_3$.—The substance crystallizes with the precautions given above in long slender needles, with a slightly yellowish tinge, which melt at 77°–78°, and are very soluble in ethyl alcohol, methyl alcohol, ether, benzol, chloroform, acetone, or glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroïn; somewhat soluble in cold water, more soluble in hot. With alkalies it forms reddish yellow salts. Strong sulphuric or hydrochloric acid does not act on it; it dissolves in strong nitric acid, but seems to be precipitated unchanged by dilution.

We also obtained a small amount of another substance with a higher melting-point, but not in sufficient quantity to characterize it.

Action of Sodic Propylate on Tribromtrinitrobenzol.

4 grams of normal propyl alcohol were mixed with anhydrous benzol, and treated with 1.5 grams of metallic sodium until all the sodium had disappeared; the reaction ran slowly, and was assisted by a gentle heat. The sodic propylate thus obtained was carefully cooled, and then a benzol-solution of 10 grams of tribromtrinitrobenzol added in small portions at a time, shaking and cooling with water after each addition. The proportions are about three atoms of sodium and three molecules of propyl alcohol to

each molecule of tribromtrinitrobenzol. As the first portions of the solutions were mixed the liquid turned blood-red, and this color, which at first faded to yellow on shaking, became permanent as more of the solution of tribromtrinitrobenzol was added. The mixture, which at no time showed a rise of temperature, was allowed to stand over night in a corked flask, and then the solution was filtered from a deposit of solid matter, which, after drying off the benzol, gave tests for a bromide and a nitrate. The benzol solution to which the solid not used for the above tests had been added was treated with water, and then acidified with dilute sulphuric acid, washed thoroughly, and, after most of the benzol had been recovered by distillation, the rest was distilled off in a current of steam. The residue thus obtained was oily, but solidified after standing for some time ; it was then purified by crystallization from alcohol until it showed the constant melting-point 109°–110°, when it was dried at about 70°, and analyzed with the following results :

0.2366 gram substance gave 0.4058 gram CO_2 and 0.1214 gram H_2O.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.78
Hydrogen	5.43	5.70

The substance gives no test for bromine when heated on a copper wire. These results prove that it is the normal propyl ether of trinitrophloroglucin.

The aqueous solution, acidified with sulphuric acid, from which the benzol had been separated gave on extraction with ether a small amount of a yellow substance, which seemed to be trinitrophloroglucin, but was not present in sufficient amount for complete identification.

Properties of the Normal Tripropyl Ether of Trinitrophloroglucin, $C_6(OC_3H_7)_3(NO_2)_3$.—This substance crystallizes in plates often as much as 3 mm. long and 1 mm. broad, which under the microscope are seen to be made up of a number of flat prisms with square ends united by their longer sides, and usually much striated on lines parallel to both sets of edges. Its color is white with a very slight yellowish tinge, and it turns yellowish brown on standing exposed to the air. It melts at 109°–110°, and is soluble in cold ethyl or methyl alcohol, more freely when hot; freely

soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; soluble in glacial acetic acid; slightly soluble in ligroïn, or in water whether hot or cold. Neither strong sulphuric, strong nitric, nor strong hydrochloric acid has any apparent action on it, whether cold or hot. The best solvent for it is boiling alcohol.

In another experiment no benzol was used, but the tribromtrinitrobenzol suspended in propyl alcohol was treated with sodic propylate. The product in this case was an oil which did not solidify even after standing for three months. We accordingly tried to purify it by treatment with a cold solution of sodic hydrate, and in this way obtained an orange solution, from which trinitrophloroglucin was easily isolated, pointing to the presence of the tripropyl ether of this body in the oil. After we could obtain no more of the sodium salt of the trinitrophloroglucin by further action of sodic hydrate, the oil was washed with water, dissolved in alcohol, precipitated again with water, and dried at 100°, when we hoped an analysis might throw some light on its composition; but in this we were disappointed, as a determination of the amount of bromine gave 45.29 per cent., whereas the tribromnitroresorcin dipropyl ether, which we hoped might have been formed, should contain 50.42 per cent. of bromine. As we could find no better way of purifying this substance, we have been forced to leave undecided the nature of the product formed by the replacement of nitro groups in tribromtrinitrobenzol by propoxy radicles. Fortunately, it is not a point of great importance.

Action of Sodic Isopropylate on Tribromtrinitrobenzol.

4 grams of isopropyl alcohol were converted into its sodium compound by treatment with 1.5 grams of sodium in anhydrous benzol, when it was found that the isopropyl alcohol acts on sodium more energetically than normal propyl alcohol, but both act less readily than ethyl alcohol. The isopropylate thus obtained was allowed to act on 10 grams of tribromtrinitrobenzol under the conditions described in the preceding section. The phenomena observed in this case were the same as those described for the normal propylate except that a slight rise of temperature from the reaction was observed. The solid deposited over night gave a strong test for sodic bromide and a distinct test for sodic nitrite.

The principal organic product was obtained and purified in the way given under the normal propyl compound until it showed the constant melting-point 130°, when it was dried at 100°, and analyzed with the following results:

0.2280 gram substance gave 0.3876 gram CO_2 and 0.1182 gram H_2O.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.36
Hydrogen	5.43	5.76

The substance gave no test for bromine when heated with cupric oxide. A small amount of trinitrophloroglucin seemed to be formed as a secondary product in preparing the substance analyzed above.

Properties of the Triisopropyl Ether of Trinitrophloroglucin, $C_6(OC_3H_7)_2(NO_2)_3$.—This substance crystallizes in plates often 1 cm. long, made up of flattened prisms united by their longer sides. These prisms are terminated by two planes at an obtuse angle to each other, and seem to belong to the monoclinic system. It is white when first prepared, but gradually takes on an orange color on exposure to the air. It melts at 130°, and is not very soluble in cold ethyl or methyl alcohol, more soluble in hot ; very soluble in benzol or chloroform ; freely in ether or acetone ; soluble in carbonic disulphide; slightly soluble in cold glacial acetic acid, freely when hot ; very slightly soluble in ligroïn, and nearly insoluble in water whether cold or hot. The three strong acids have no apparent action on it whether cold or hot. The best solvent for it is boiling alcohol.

Action of Sodic Benzylate on Tribromtrinitrobenzol.

The sodic benzylate used was prepared as follows: To 1.3 grams of sodium mixed with anhydrous benzol and heated in a flask with a return-condenser, 6.5 grams of benzyl alcohol were added in small quantities at a time, and the heating continued until all the sodium had disappeared, which usually was not till after four hours. The benzyl alcohol therefore acts with sodium much more slowly than any of the other alcohols used by us. In this way we obtained a benzol solution of the sodic benzylate,[1]

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[1] Since this part of our work was finished, Brühl and Biltz have published similar observations on other alcoholates in Ber. d. chem. Ges. **21**, 649 (1891).

which remained clear after it had cooled until it was shaken, when the solid separated in a gelatinous state. To the mixture of gelatinous sodic benzylate and benzol thus obtained a benzol-solution of 9 grams of tribromtrinitrobenzol was added; that is, for each molecule of tribromtrinitrobenzol we used three molecules of sodic benzylate.[1] The mixture was allowed to stand in the cold over night, the orange-red solution thus formed evaporated to dryness on a steam radiator at temperatures below 70°, and the residue washed with water and afterward with alcohol, after which it was purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting-point 171°. The analyses of the substance dried at 100° gave the following results:

I. 0.2038 gram substance gave 0.4546 gram CO_2 and 0.0752 gram H_2O.

II. 0.2678 gram substance gave 18.8 cc. N at 25° and 765.3 mm.

	Calculated for $C_6(OC_7H_7)_5(NO_2)_3$.	I.	Found. II.
Carbon	61.01	60.84	...
Hydrogen	3.96	4.10	...
Nitrogen	7.91	...	7.89

The substance gave no test for bromine when heated with cupric oxide.

10 grams of tribromtrinitrobenzol gave only 1.5 grams of the tribenzyl ether of trinitrophloroglucin, the analysis of which is given above, that is, less than 13 per cent. of the theoretical yield. This substance, therefore, is not by any means the principal product of the reaction. What the other products are will be discussed after the description of the properties of the benzyl ether.

Properties of the Trinitrophloroglucin Tribenzyl Ether.—This substance crystallizes from a mixture of alcohol and benzol in slender white needles forming a thick mat. It turns yellowish brown on exposure to the air, and melts at 171°; is slightly soluble even in hot alcohol, less soluble still in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform or acetone; freely in carbonic disulphide; soluble in glacial acetic acid; very slightly soluble in ligroïn; essentially insoluble in water, whether cold or hot. The best solvent for it is a mixture

[1] The same principal product was obtained in a subsequent experiment with only two molecules of sodic benzylate. In most cases a slight excess of benzyl alcohol was used.

of alcohol and benzol. Strong sulphuric acid does not seem to act on it until charring sets in; strong nitric acid does not act on it in the cold, but seems to oxidize it when hot; strong hydrochloric acid has no apparent action on it, hot or cold.

Other Products of the Action of Sodic Benzylate on Tribrom-trinitrobenzol.—To obtain these substances the aqueous and alcoholic washings mentioned above were evaporated to dryness, and the oily portion separated by extraction with a little alcohol from the salts. These, it was found, were a mixture of the sodium salt of trinitrophloroglucin with sodic bromide and nitrite, from which the trinitrophloroglucin was easily obtained, and identified by the melting-point 167°, and by analysis. It is one of the principal products of the reaction, and in fact most of the trinitrophloroglucin used for the analyses given in the first part of this paper was obtained in this way.

The oily material separated by the alcohol consisted mostly of the excess of benzyl alcohol, but on warming it we perceived the smell of benzyl bromide, and also suffered from its violent action on the eyes. Accordingly some of it, carefully washed to remove any sodic bromide, was boiled with an alcoholic solution of sodic sulphide, when it gave a strong smell of benzyl sulphide, and the water with which it was washed gave a faint test for bromine with chlorine-water. We did not succeed, however, in isolating the benzyl sulphide, which at best must have been present in very small quantity. Another similar oil, after thorough washing with water, was boiled with sodic acetate and alcohol, then water was added, which after being freed from the organic matter gave a slight test for bromine with chlorine-water. In another experiment the original product, after acidification with dilute sulphuric acid, was distilled with steam, and the oily distillate, having been thoroughly washed with water, was boiled with alcoholic sodic acetate, when it yielded a very strong test for a bromide with chlorine-water. These experiments have convinced us that in these three preparations a small quantity of benzyl bromide was present in the product of the reaction, although we have not succeeded in isolating the benzyl bromide itself, or one of its derivatives. This did not proceed from an impurity of benzyl bromide in the benzyl alcohol used, since after boiling it with an alcoholic solution of sodic acetate no test for sodic bromide could be obtained; it must have been formed, therefore, either in the course

of the reaction, or in the subsequent processes of purification. It is barely possible that this latter supposition may account for it in the last case, where the strongest test for bromine was obtained, as this was acidified before distillation with steam, and hydrobromic acid produced by the sulphuric acid and sodic bromide might have converted some of the excess of benzyl alcohol into benzyl bromide, although this seems highly improbable, because the solution was kept throughout in a very dilute state. In the two previous cases, however, this explanation cannot apply, as no acid whatever had been added, so that no hydrobromic acid could have been formed; we are forced therefore to assume that the benzyl bromide was formed by the direct reaction and not by a secondary one, and under these circumstances the following reaction is the only one which seems to us admissible:

$$3C_7H_7ONa + C_6Br_3(NO_2)_3 = C_6(ONa)_3(NO_2)_3 + 3C_7H_7Br.$$
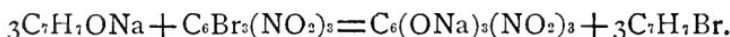
This is certainly very improbable, and we should add that, when we tried to confirm it by a repetition of the experiment, we did not succeed in detecting any benzyl bromide in the product. At first sight it would seem that a reaction the reverse of that given above would be more probable, but we proved that this was not the case by a special experiment, which showed that benzyl bromide had no action on the sodium salt of trinitrophloroglucin under the conditions used by us. We may add that amyl bromide also has no action under these conditions. On the other hand, there is little doubt that the benzyl bromide, if formed by this reaction, would act on the sodic benzylate forming benzyl ether. Accordingly, we tried to isolate benzyl ether from the oily product of the reaction by distilling off the excess of benzyl alcohol; there was so little of the residue which did not pass over at 207° that it was impossible to purify it properly; such as it was, however, it gave results on analysis agreeing with those calculated for benzyl alcohol (carbon, 76.70 instead of 77.78). We conclude, therefore, that if the reaction given above takes place, it is only to a very moderate extent, the principal reaction being the formation of the trinitrophloroglucin tribenzyl ether, which was then more or less saponified by the sodic hydrate formed by the action of atmospheric moisture on the sodic benzylate. We have not succeeded in detecting the organic substance formed by the removal of one or more nitro groups, as indicated by the appearance of sodic nitrite among the products.

Sodic Isobutylate or *Sodic Isoamylate* acted with tribromtrinitrobenzol in the same way as the alcoholates already mentioned, but the organic products insoluble in water were oily, and we did not succeed in isolating any compounds fit for analysis from them. The aqueous filtrates contained a considerable amount of the sodium salt of trinitrophloroglucin. As the subject was not of sufficient interest to repay extended work, it was abandoned.

Quantitative Study of the Action of other Alcoholates on Tribromtrinitrobenzol.

The object of this work was to make a comparison between the actions of sodic ethylate and of other alcoholates on tribromtrinitrobenzol, and for this purpose we selected the quantitative determination of the amounts of sodic nitrite formed by the reaction, since our results with the ethylate had shown that the percentage of nitrogen removed as sodic nitrite was essentially constant under the conditions used by us. The amount of bromide formed was also determined in most cases, although of little value for purposes of comparison. Accordingly the following determinations were made, the results of which, with those from sodic ethylate already described, are given together in tabular form after the descriptions of the determinations. To economize our alcohols, as we had but a small stock of some of them, we have used principally the method with benzol as a solvent.

Experiments in which the Alcohol was the only Solvent.

XIV. Weight taken, 1.0578 grams. Alcoholate used, *sodic methylate*. Weight of aqueous solution, 115.1 grams. 54.3 grams solution gave 13.6 cc. N from $NaNO_2$ at 18° and 758.9 mm. 60.8 grams solution gave 0.3768 gram AgBr.

XV. Weight taken, 1.157 grams. Alcoholate used, *sodic propylate*. Weight of aqueous solution, 92 grams. 54.1 grams solution gave 13 8 cc. N from $NaNO_2$ at 16° and 775.4 mm.

XVI. Weight taken, 1.1582 grams. Alcoholate used, *sodic isobutylate*. Weight of aqueous solution, 117.5 grams. 33.1 grams solution gave 5.25 cc. N from $NaNO_2$ at 16° and 765.5 mm. 43.3 grams solution gave 0.2390 gram AgBr.

XVII. Weight taken, 1.2696 grams. Alcoholate used, *sodic isobutylate*. Weight of aqueous solution, 56.65 grams. 19.3 grams solution gave 9.4 cc. N from $NaNO_2$ at 29.5° and 756.3 mm. 15.95 grams solution gave 0.2198 gram AgBr.

XVIII. Weight taken, 1.5118 grams. Alcoholate used, *sodic isoamylate.* Weight of aqueous solution, 53.3 grams. 26.5 grams solution gave 8.4 cc. N from $NaNO_2$ at 20° and 762.4 mm. 26.25 grams solution gave 0.3352 gram AgBr.

XIX. Weight taken, 1.5656 grams. Alcoholate used, *sodic isoamylate.* Weight of aqueous solution, 85.1 grams. 37.4 grams solution gave 9.9 cc. N from $NaNO_2$ at 19.5° and 766.2 mm.

Action of Sodic Methylate in Benzol.

XX. Weight taken, 1.0892 grams. Weight of solution, 65.7 grams. 31.7 grams solution gave 10.1 cc. N from $NaNO_2$ at 22° and 766.9 mm. 34 grams gave 0.4212 gram AgBr. Organic matter insoluble in water, 0.509 gram.

XXI. Weight taken, 1.2612 grams. Weight of aqueous solution, 40.05 grams. 17.35 grams solution gave 11.7 cc. N from $NaNO_2$ at 25° and 758.9 mm. 22.7 grams solution gave 0.4088 gram AgBr.

XXII. Weight taken, 1.1561 grams. Weight of aqueous solution, 58.9 grams. 24.3 grams solution gave 10.9 cc. N from $NaNO_2$ at 25.5° and 765.4 mm. 34.6 grams solution gave 0.4732 gram AgBr.

Action of Normal Sodic Propylate in Benzol.

XXIII. Weight taken, 1.2281 grams. Weight of aqueous solution, 60.85 grams. 22.75 grams solution gave 8.2 cc. N from $NaNO_2$ at 20.5° and 759.4 mm. 38.1 grams solution gave 0.1398 gram AgBr.

XXIV. Weight taken, 1.297 grams. Weight of aqueous solution, 71.6 grams. 19.6 grams solution gave 4.6 cc. N from $NaNO_2$ at 30° and 767 mm. 52 grams solution gave 0.7827 gram AgBr.

Action of Sodic Isopropylate in Benzol.

XXV. Weight taken, 1.3434 grams. Weight of aqueous solution, 50.15 grams. 20 grams solution gave 5.9 cc. N from $NaNO_2$ at 24.5° and 762.5 mm. 30.15 grams solution gave 0.2679 gram AgBr.

Action of Sodic Isobutylate in Benzol.

XXVI. Weight taken, 1.1598 grams. Weight of aqueous solution, 59 05 grams. 27.05 grams solution gave 5.2 cc. N from $NaNO_2$ at 23.5° and 759.2 mm. 32 grams solution gave 0.303 gram AgBr.

XXVII. Weight taken, 1.1551 grams. Weight of aqueous solu-

tion, 79.5 grams. 22.05 grams solution gave 4.2 cc. N from $NaNO_2$ at 27° and 764.5 mm. 57.45 grams solution gave 0.722 gram AgBr.

Action of Sodic Isoamylate in Benzol.

XXVIII. Weight taken, 1.4427 grams. Weight of aqueous solution, 85.55 grams. 31.7 grams solution gave 5.7 cc. N from $NaNO_2$ at 23° and 760.9 mm. 40.65 grams solution gave 0.4184 gram AgBr.

XXIX. Weight taken, 1.4485 grams. Weight of aqueous solution, 106.65 grams. 33 6 grams solution gave 5.3 cc. N from $NaNO_2$ at 25 5° and 764.2 mm. 73.05 grams solution gave 0.8515 gram AgBr.

Action of Sodic Benzylate in Benzol.

XXX. Weight taken, 1.0747 grams. Weight of aqueous solution, 92.2 grams. 33.5 grams solution gave 2.7 cc. N from $NaNO_2$ at 30.5° and 758.8 mm. 58.7 grams solution gave 0.5584 grams AgBr.

Action of Sodic Phenylate in Benzol.

XXXI. Weight taken, 1.1227 grams. Weight of aqueous solution, 67.15 grams. 32.5 grams solution gave 3 cc. N from $NaNO_2$ at 29° and 766.5 mm. 30.05 grams solution gave 0.1568 gram AgBr.

The results of these experiments are collected in Tables III and IV with those previously given by sodic ethylate. The first column contains the sort of alcohol used and the number of the experiment, the second the weight of tribromtrinitrobenzol used, the third the percentage of nitrogen, and the fourth the percentage of bromine removed, calculated in the way already described in connection with Tables I and II.

TABLE III.—*Experiments with the Alcohol alone.*

Sort of Alcohol used.		Weight of Tribromtrinitrobenzol.	Percentage of Nitrogen.	Percentage of Bromine.
Methyl	XIV	1.0578	50.52	53.79
Ethyl	I	10.556	45.88	42.53
	II	10.1582	44.85	36.67
	III	1.0366	46.95	42.85
	IV	10.	46.86	39.39
	V	10.	45.06	18.02
Propyl	XV	1.157	38.80	...
Isobutyl	XVI	1.1582	30.40	44.69
	XVII	1.2696	37.83	49.04
Isoamyl	XVIII	1.5118	20 62	36.16
	XIX	1.5656	26.73	...

TABLE IV.—*Experiments with Alcohol and Benzol.*

Sort of Alcohol used.		Weight of Tribromtrinitrobenzol.	Percentage of Nitrogen.	Percentage of Bromine.
Methyl	XX	1.089	35.28	59.62
	XXI	1.261	38.37	45.64
	XXII	1.156	41.17	55.59
Ethyl	VI	10.022	33.58	59.54
	VII	10.1976	33.09	38.91
	VIII	1.2524	33.03	74.32
	IX	1.2682	33.31	66.21
	X	1.2287	34.42	49.10
Propyl	XXIII	1.2281	32.74	14.51
	XXIV	1.297	22.83	66.30
Isopropyl	XXV	1.3434	19.87	26.46
Isobutyl	XXVI	1.1598	17.68	38.46
	XXVII	1.1551	23.41	69.01
Isoamyl	XXVIII	1.4427	19.33	48.70
	XXIX	1.4485	20.89	68.50
Benzyl	XXX	1.0747	12.00	65.09
Phenol	XXXI	1.1227	9.78	24.90

An examination of Tables III and IV shows that the percentages of nitrogen obtained with the ethylate are the only ones which agree among themselves, the numbers with other alcoholates often differing by about six per cent.—in one case by nearly ten per cent. Under these circumstances it is obviously unwise to attempt to draw any definite inferences from these results; we therefore dismiss them with the general remark that the amount of nitrogen removed seems to show a tendency to diminish as the molecular weight of the alcohol increases.

The length of time during which the mixture of tribromtrinitrobenzol and the alcoholate stood seemed to have but little influence on the reaction, as is shown by Experiments V, XXIV, XXVII, and XXIX, in which the mixture stood one or more days longer than the eighteen hours used for the other experiments. In fact, longer standing could not have any great effect in the case of the ethylate, as in eighteen hours eighty to ninety per cent. of the tribromtrinitrobenzol had entered into the reactions. With the higher alcoholates this was not the case, and it may be that the action had not reached its end in eighteen hours, and that the variation observed in the percentages was due to differences in the

times of reaction; but some experiments, in which the mixtures were allowed to stand a longer time in order to test this point, gave unsatisfactory results, apparently on account of the oxidation of the sodic nitrite formed by the oxygen of the air.

PART III.—ACTION OF SODIC ETHYLATE ON CERTAIN DERIVATIVES OF TRIBROMTRINITROBENZOL CONTAINING ALKYLOXY RADICLES.

Action of Sodic Ethylate on the Triphenyl Ether of Trinitrophloroglucin.

This work was undertaken in the hope that the triphenyl ether of trinitrophloroglucin, $C_6(OC_6H_5)_3(NO_2)_3$, might behave toward sodic ethylate like tribromtrinitrobenzol, that is, lose one or more nitro groups as sodic nitrite, which would be replaced by the ethoxy group. This hope, however, has not been fulfilled, as instead of the nitro groups the phenoxy radicles are removed by the sodic ethylate, becoming replaced by ethoxy groups, while sodic phenylate is formed. The experiments were carried on as follows: 2.5 grams of the triphenyl ether of trinitrophloroglucin[1] dissolved in benzol were mixed with the sodic ethylate from 0.4 gram of sodium, and the bright red mixture allowed to stand two or more hours in the cold. After this it was allowed to evaporate spontaneously, and the residue warmed with water on the steambath, when most of it dissolved. The insoluble portion was purified by crystallization from alcohol until it showed the constant melting-point 119°–120°, which indicated that it was trinitrophloroglucin triethyl ether, and this was proved to be the case by the following analysis:

0.2080 gram substance gave 22.5 cc. N at 21° and 759.3 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.[2]
Nitrogen	12.17	12.30

The aqueous filtrate which contained the other products of the reaction besides the trinitrophloroglucin triethyl ether gave no

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[1] In preparing this substance from tribromtrinitrobenzol again we have found that a tolerable excess of sodic phenylate should be used in order to avoid the formation of a compound containing bromine, — $C_6(OC_6H_5)_2Br(NO_2)_3$ probably. With such an excess, the reaction runs without heat, and is complete in a few minutes. We have not observed the green color noticed by us last year (this Journal **13**, 189), which must therefore have been due to some impurity.

[2] This analysis has also been given earlier in this paper, where the composition of the triethyl ether is first determined.

test for sodic nitrite, even with starch-paste, potassic iodide, and sulphuric acid. It was acidified with dilute sulphuric acid and extracted with ether, which left an oily substance solidifying after some time, and smelling strongly of phenol. To prove that this was phenol, it was dissolved in a large quantity of water and bromine-water added to the solution, which gave a white precipitate melting constantly, after crystallization from dilute alcohol, at 92°, the melting-point given by Post for tribromphenol; as, however, both Körner and Sintenis give 95°, we thought it necessary to analyze the substance, which was done with the following result:

0.2803 gram substance gave by Carius' method 0.4748 gram AgBr.

	Calculated for $C_6H_2Br_3OH$.	Found.
Bromine	72.51	72.07

There can be no doubt, therefore, that the substance is tribromphenol, and that the action of the sodic ethylate upon trinitrophloroglucin triphenyl ether takes place according to the following reaction:

$$C_6(OC_6H_5)_3(NO_2)_3 + 3NaOC_2H_5 =$$
$$C_6(OC_2H_5)_3(NO_2)_3 + 3NaOC_6H_5.$$
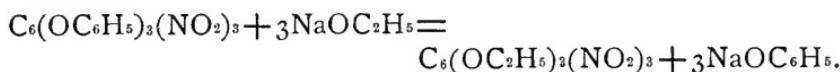
The bright red color observed in the solution was undoubtedly due to some of the sodium salt of trinitrophloroglucin formed by the action of the small amount of sodic hydrate, which it is almost impossible to exclude from sodic ethylate owing to the hygroscopic nature of absolute alcohol.

This decomposition of the trinitrophloroglucin triphenyl ether by sodic ethylate calls to mind the behavior of esters with another alcohol and a small quantity of an alcoholate, as studied by Purdy[1] and Peters,[2] especially as our ether approaches the esters on account of the marked acid properties of the trinitrophloroglucin. Kossel and Krüger[3] have also found that sodic ethylate converts salol into salicylic ester (or acid), and sodic phenylate, and that glycerids are decomposed by sodic ethylate in a similar way, a result which is confirmed by Obermüller.[4]

Action of Sodic Ethylate on Tribromnitroresorcin Diethyl Ether.

Early in our work with the tribromnitroresorcin diethyl ether melting at 101° we noticed that, although it was not acted on by a

[1] Ber. d. chem. Ges. **20**, 1554.   [2] Ann. Chem. (Liebig) **257**, 353.
[3] Ztschr. physiol. Chem. **15**, 321.   [4] *Ibid.* **16**, 152.

cold solution of sodic ethylate in alcohol, it was attacked if heated
with such a solution, but our attempts to study this reaction were
baffled for a long time by the difficulty in removing from the crys-
talline product the large amount of tarry matter which was formed
at the same time, even constituting almost the whole of the mass,
if the heat was not applied cautiously. After many experiments
we succeeded in obtaining a satisfactory result by proceeding as
follows : 13 grams of tribromnitroresorcin diethyl ether were cov-
ered with absolute alcohol, and an alcoholic solution of sodic
ethylate added. The flask containing the mixture was, after fitting
it to a return-condenser, immersed in a beaker of cold water, which
was heated slowly. As the temperature rose the substance went
into solution with a pale reddish color, and in a few minutes after
that there was a sudden change, the solution becoming almost
black, although the reaction was not at all violent. At this point
the heating must be stopped to avoid the formation of a large
quantity of the tarry impurity. The contents of the flask, which
had a peculiar aromatic odor not belonging to the compound we
have isolated, was allowed to evaporate to dryness spontane-
ously, and the residue washed several times with cold water, which
was found to contain sodic bromide. The water left undissolved
a most unpromising tarry mass with almost no sign of crystalline
form, but by extracting it with hot ligroïn a crystalline substance
was obtained, which was purified by repeated crystallization from
hot alcohol with the aid of bone-black until it melted constant at
115°, when it was dried at 100° and analyzed with the following
results :

I. 0.1897 gram substance gave 0.2874 gram CO_2 and 0.0782
gram H_2O.

II. 0.1519 gram substance gave by Carius' method 0.0985 gram
AgBr.

	Calculated for $C_5H_2BrNO_2(OC_2H_5)_2$.	Found. I.	II.
Carbon	41.38	41.31	...
Hydrogen	4.14	4.58	...
Bromine	27.58	...	27.60

The substance has therefore been formed from the tribromnitro-
resorcin diethyl ether by the replacement of two atoms of bromine
by two of hydrogen, a reaction which is similar in principle to the
replacement of the bromine by hydrogen in bromdinitroresorcin

diethyl ether, when treated with a boiling solution of sodic ethylate in alcohol, and to the similar replacements of bromine by hydrogen in the formation of bromdinitrophenylmalonic ester and related substances from tribromdinitrobenzol and tribromtrinitrobenzol.

Properties of Bromnitroresorcin Diethyl Ether, $C_6H_2BrNO_2(OC_2H_5)_2$.

The substance crystallizes from hot alcohol in long radiating silky white needles, which melt at 115°, and are soluble in cold alcohol, more freely in hot; freely soluble in cold methyl alcohol; very freely in benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ligroïn, much more soluble in hot; essentially insoluble in water. Neither hydrochloric, nitric, nor sulphuric acid seems to have any action on it, and the same is the case with a solution of sodic hydrate.

LXXX.—ON THE CUPRIAMMONIUM DOUBLE SALTS.[1]

By Theodore William Richards and Hubert Grover Shaw.

In the course of an extended investigation upon the ammoniacal compounds of copper, undertaken with the hope of obtaining more light upon the vexed question of their structure, a new class of interesting compounds was discovered. The preliminary notice of these compounds was published about a year ago;[2] but since that time several new ones have been added to the list. It is the object of this paper more fully to describe all of these substances, so far as they have been studied.

The generic feature of the new class is the fact that two different acids—a halogen and an organic acid radicle—are united at the same time to the ordinary cupriammonium group. Below are tabulated the formulæ of the compounds, the preparation, properties, and analyses of which are described in the work which follows :

(1.) $Cu(NH_3)_2BrC_2H_3O_2$.
(2.) $Cu(NH_3)_3ClC_2H_3O_2.H_2O$.
(3.) $[Cu(NH_3)_2ClC_2H_3O_2]_2.3NH_4C_2H_3O_2 + 7H_2O$.
(4.) $Cu(NH_3)_2BrCHO_2$.

[1] Presented at a meeting of the American Academy of Arts and Sciences, held May 10, 1893.
[2] Theodore W. Richards: Ber. d. chem. Ges. **25**, 1492. Since the publication of this paper, F. Foerster has announced the discovery of cupriammonium acetate (*Ibid.* **25**, 3416).

Besides these compounds two others, which appeared as by-products of the investigation, are worthy of description :

(5.) $CuCl_2.2NH_4C_2H_3O_2$.

(6.) $3CuBr_2.10NH_3$.
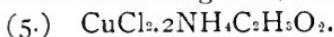
1. *Cupriammonium Acetobromide*, $Cu(NH_3)_2BrC_2H_3O_2$.—This compound is formed with great ease whenever cupric bromide is treated with alcohol and saturated with ammonia-water, and the mixture is nearly neutralized with strong acetic acid. For example, 5 grams cupric bromide were shaken with 10 cc. alcohol and the like volume of saturated ammonia-water, until all of the copper was converted into cupriammonium bromide. The bright blue precipitate was then immediately dissolved in 60–70 cc. additional alcohol, and 16 cc. strong acetic acid. Upon cooling the solution, and allowing it slowly to evaporate in the air, large brilliant deep-blue crystals which apparently belong to the monoclinic system, slowly separated.[1]

The same substance may be obtained in a similar manner from cupric acetate and ammonic bromide, after treating with ammonia and afterwards with acetic acid.

The new compound is only very slightly soluble in pure alcohol, and is decomposed at once by water into impure cupric hydroxide, ammonic acetate and ammonic bromide. The cupric hydroxide contains large amounts of basic cupric bromide and acetate.

The only satisfactory solvent for it seems to be a strong aqueous solution of ammonic acetate and bromide, containing more or less alcohol. By this singular mixture the compound is not decomposed, even at 70° or 80° C. Acids of course at once decompose and dissolve cupriammonium acetobromide, and alkalies upon boiling set free ammonia and precipitate cupric oxide as usual. The crystals are fairly permanent in the air ; they are singularly brittle and rather light, possessing a specific gravity of 2.134.

In the analysis of the compound, copper was determined electrolytically after evaporation with sulphuric and nitric acids ; and the bromine and ammonia were determined as usual. The accurate determination of the acetic acid was a much harder task. Distillation with phosphoric acid, according to the method recommended by Fresenius,[2] is not very satisfactory because of the great expenditure of time which it requires, and the fact that

[1] T. W. Richards: Ber. d. chem. Ges. **23**, 3791.
[2] Ztschr. anal. Chem. **5**, 315; **14**, 172.

traces of hydrobromic and phosphoric acids are always found in the distillate. Usually the two acids were precipitated together from the neutralized distillate, and the result was calculated as argentic bromide; but in some cases they were determined separately. The presence of phosphoric acid in the distillate is especially unfortunate, because of the uncertainty which it introduces in the end-point of the alkalimetric reaction.

On the other hand, quantitative combustion after the usual method, and calculation of the acetic acid from the carbon dioxide formed, is not easy because of the presence of the large amount of bromine.

Analyses of $Cu(NH_3)_2BrC_2H_3O_2$.

I. 0.0685 gram substance yielded 0.01865 gram Cu upon electrolysis.

II. 0.1446 gram substance distilled with KOH required 12.16 cc. decinormal acid solution for neutralization.

III. 0.08485 gram substance yielded 0.06705 gram AgBr.

IV. 0.3173 gram substance yielded 0.2518 gram AgBr.

V. The distillate from a mixture of phosphoric acid and 0.2311 gram substance required 10.11 cc. decinormal alkali for neutralization. Approximately corrected for alkalimetric equivalent of Ag_3PO_4 and AgBr obtained from distillate this amount becomes 9.90.

Many other analyses were made of subsequent preparations, in order to be sure of the identity of the crystals prepared in different ways. It is considered unnecessary to publish these, since they agreed essentially with those given above.

No.	Cu.	NH_3.	Br.	$C_2H_3O_2$.
I.	27.23	...	...	...
II.	...	14.35	...	...
III.	...	...	33.63	...
IV.	...	...	33.78	...
V.	...	...	...	25.27
Average,	27.23	14.35	33.70	25.27

	Calculated for $Cu(NH_3)_2BrC_2H_3O_2$.	Found (Mean).
Cu	26.87	27.23
NH_3	14.42	14.35
Br	33.79	33.70
$C_2H_3O_2$	24.92	25.27
	100.00	100.55

2. *Ammon-cupriammonium Acetochloride,* $Cu(NH_3)_3ClC_2H_3O_2$.-H_2O.—Almost any mixture which brings together in concentrated solution copper, chlorine, much acetic acid, and an excess of ammonia yields ammon-cupriammonium acetochloride upon the addition of alcohol. The substance consists of brilliant blue scales, having a pearly luster. These crystals lose ammonia and water slowly upon exposure to the air, with marked alteration of color; they are decomposed by water, a small amount of the copper going into solution. For analysis the crystals were pressed between layers of filter-paper as rapidly as possible. A bromine compound similar in every respect to this one has been prepared, and will form the subject of a future communication.

Analyses of Ammon-Cupriammonium Acetochloride.

I. 0.2524 gram substance yielded on electrolysis 0.0698 gram Cu.

II. 0.2273 gram substance yielded 0.0634 gram Cu.

III. 0.2875 gram substance yielded 0.0808 gram Cu.

IV. 0.1337 gram substance required on distillation 17.37 cc. decinormal acid to neutralize ammonia volatilized.

V. 0.1554 gram substance required in the same way 20.17 cc. acid.

VI. 0.0979 gram substance required 12.56 cc. decinormal acid.

VII. 0.2708 gram substance yielded 0.1704 gram AgCl.

VIII. 0.2696 gram substance yielded 0.1700 gram AgCl.

IX. 0.1926 gram substance yielded upon distillation with phosphoric acid a distillate requiring 8.94 cc. decinormal baric hydroxide for neutralization with phenol phthaleïn. This liquid yielded 0.0116 gram AgCl, containing traces of Ag_3PO_4, which amount is equivalent to about 0.81 cc. decinormal acid. Hence the acetic acid in the distillate must have required 8.13 cc. alkaline solution.

X. 0.2215 gram substance required upon distillation 10.38 cc. baric hydrate, of which 0.66 were required to neutralize HCl corresponding to 0.0096 gram AgCl obtained from the neutralized distillate ($10.38 - 0.66 = 9.72$).

No.	Cu.	NH_3.	Cl.	$C_2H_3O_2$.
I.	27.65	...	...	...
II.	27.89	...	...	...
III.	28.17	...	...	...
IV.	...	22.16	...	...

No.	Cu.	NH₃.	Cl.	C₂H₃O₂.
V.	...	22.14	...	...
VI.	...	21.89	...	...
VII.	...	...	15.56	...
VIII.	...	...	15.59	...
IX.	...	...	...	24.91
X.	...	...	...	25.90
Average,	27.90	22.06	15.57	25.40

The averaged results are given below.

	Calculated for $Cu(NH_3)_3ClC_2H_3O_2H_2O$.	Found.
Cu	27.98	27.90
NH₃	22.53	22.06
Cl	15.60	15.57
C₂H₃O₂	25.97	25.40
H₂O (by difference)	7.92	9.07
	100.00	100.00

3. *Complex[1] Cupriammonium Acetochloride*, $[Cu(NH_3)_2ClC_2H_3O_2]_2.3NH_4C_2H_3O_2 + 7H_2O$.—The complex cupriammonium acetochloride is obtained under conditions which would have been expected to produce the simple compound enclosed in the brackets above. This simple compound, probably owing to its great solubility, we have been unable as yet to isolate. Whenever cupric chloride is treated with a great excess of concentrated ammonia-water, the excess cautiously neutralized with glacial acetic acid, and the whole treated with alcohol and allowed to evaporate, great crystals of the complicated compound containing three molecules of ammonic acetate and probably seven of water to every two of cupriammonium acetochloride always separate out. The addition of somewhat more acetic acid in this case constitutes the sole difference between the methods of preparing this compound and the preceding. In the former case an excess of ammonia was required.

The crystals of the complex salt are of a most brilliant blue with a tinge of violet, and may be obtained of almost any size. They dissolve in very small amounts of water without apparent decompo-

[1] "Complex" is used here in default of a word more capable of describing the complexity of the compound. It is not intended to carry with it any technical meaning with regard to the structure of the molecule. Indeed, the names of all the compounds described in this paper are far from satisfactory to us; they would be thrown out very gladly if better ones could be found.

sition, but larger amounts of water decompose them. The new compound readily loses water and ammonic acetate in the air, and is converted into a pale green powder, which remains to be investigated. Over caustic potash in a desiccator, on the contrary, it is soon converted into a pale violet powder with a very sudden loss of weight. After the sudden decrease has stopped a slower decrease continues, without change of color, and the composition of the powder constantly approaches that of the simple cupriammonium acetochloride. Its complete conversion into this compound we have not yet been able to accomplish; and regarding the exact nature of the compounds which are marked by the irregular decrease in weight we have as yet nothing to say.

For analysis the crystals were pressed between layers of filter-paper. The possible causes of error from decomposition on the one hand, and the adhesion of mother-liquor on the other, were guarded against as much as possible. Nevertheless these causes of error are undoubtedly responsible for the not unreasonable variations noticeable in the analytical results; for the three specimens of crystals analyzed were undoubtedly identical.

Analyses of Complex Cupriammonium Acetochloride.

I. 0.2404 gram substance yielded on electrolysis 0.0411 gram Cu.

II. 0.2446 gram substance yielded on electrolysis 0.0419 gram Cu.

III. 0.2772 gram substance yielded on electrolysis 0.0476 gram Cu.

IV. 0.1418 gram substance yielded on distillation $NH_3 = 13.25$ cc. decinormal acid.

V. 0.1403 gram substance required on distillation 13.24 cc. decinormal acid.

VI. 0.1895 gram substance required on distillation 17.79 cc. decinormal acid.

VII. 0.1472 gram substance required on distillation 14.19 cc. decinormal acid.

VIII. 0.2319 gram substance yielded 0.0895 gram AgCl.

IX. 0.2244 gram substance yielded 0.0870 gram AgCl.

X. 0.1679 gram substance gave on combustion 0.0998 gram CO_2.

No.	Cu.	NH_3.	Cl.	$C_2H_3O_2$.
I.	17.10	...	...	...
II.	17.13	...	...	...
III.	17.17	...	...	...
IV.	...	15.95	...	...
V.	...	16.11	...	...
VI.	...	16.03	...	...
VII.	...	16.46	...	...
VIII.	...	...	9.54	...
IX.	...	...	9.59	...
X.	...	...	...	39.95
Average,	17.13	16.16	9.57	39.95

	Calculated for $Cu_2(NH_3)_4Cl_2(C_2H_3O_2)_6(NH_4)_3.7H_2O$.	Found (Mean).
Cu	17.12	17.13
Cl	9.55	9.57
NH_3	16.08	16.16
$C_2H_3O_2$	39.73	39.95

A fourth sample, which had a similar appearance, was found to contain 17.61 per cent. of copper and 9.94 of chlorine. This had probably begun to lose water and ammonic acetate. A finely powdered specimen kept for eleven months over sodic hydrate was found to contain 25.8 per cent. of copper and 14.35 of chlorine. Since the theoretical percentages corresponding to $Cu(NH)_2ClC_2$ H_3O_2 are respectively 33.08 and 18.45, it is clear that the excess of ammonic acetate had not been wholly decomposed during the long exposure. Further experiments in this direction will be made in the near future.

4. *Cupriammonium Formibromide*, $Cu(NH_3)_2BrCHO_2$.—Cupriammonium formibromide is made after a method essentially similar to that employed in making the corresponding compound of acetic acid. The salt is more difficult to obtain in a pure state; but any reasonably concentrated solution containing bromine, copper, much formic acid, and ammonia in very slight excess, will deposit the deep " robin's-egg " blue crystals of the desired salt upon the addition of alcohol. The possibility of the formation of basic salts of copper is diminished if the excess of ammonia is added after the addition of the alcohol. The salt possesses no unexpected properties, except that the color of the short needles

is much less briliant and crude than that of cupriammonium aceto-bromide.

A similar compound containing chlorine instead of bromine has been prepared, and analyzed with results which were sufficiently accurate to show the analogy of the compound ; but it was thought desirable to study more carefully the conditions necessary for its preparation in a pure state before publishing the results. Moreover, a more complex formibromide of most interesting aspect and composition has been made. This substance also awaits further study.

Analyses of Cupriammonium Formibromide.

I. 0.2192 gram substance gave on electrolysis 0.0621 gram Cu.

II. 0.2164 gram substance yielded on electrolysis 0.0618 gram Cu.

III. 0.1386 gram substance yielded $NH_3 = 12.32$ cc. of decinormal acid.

IV. Similarly 0.1180 gram substance required 10.46 cc. decinormal acid.

V. 0.1599 gram substance gave 0.1371 gram AgBr.

VI. 0.2414 gram substance gave 0.2063 gram AgBr.

VII. 0.1678 gram substance gave 0.1429 gram AgBr.

VIII. 0.2062 gram substance yielded on combustion 0.0403 gram CO_2.

IX. 0.2435 gram substance yielded on combustion 0.0469 gram CO_2.

No.	Cu.	NH_3.	Br.	CHO_2.
I.	28.30	...	...	...
II.	28.56	...	...	...
III.	...	15.17	...	...
IV.	...	15.13	...	...
V.	...	...	36.49	...
VI.	...	...	36.37	...
VII.	...	...	36.24	...
VIII.	...	...	...	19.93
IX.	...	...	...	19.70
Average,	28.43	15.15	36.37	19.80

These analyses were made from several different samples (especially V, VI, and VII, which were all different), and hence they

prove the definiteness of the compound. The average results are given below.

	Calculated for Cu(NH₃)₂BrCHO₂.	Found.
Cu	28.56	28.43
NH₃	15.33	15.15
Br	35.90	36.37
CHO₂	20.21	19.80
	100.00	99.75

5. *Cupric Ammonic Acetochloride*, CuCl₂.2NH₄C₂H₃O₂.—Upon several occasions during the investigation just described, when concentrated solutions of approximately equivalent amounts of cupric chloride and ammonic acetate had been allowed to evaporate together, especially with addition of alcohol, bright green, almost cubical, crystals separated. These crystals were sometimes found to be mixed with small amounts of ammonic chloride, and sometimes almost pure. The substance is a double salt, and not a cupriammonium compound; hence it dissolves in water without apparent decomposition. The purest crystals gave the following analytical results:

I. 0.3132 gram substance gave 0.0689 gram Cu.
II. 0.2649 gram substance gave 0.0585 gram Cu.
III. 0.1180 gram substance gave 0.1181 gram AgCl.
IV. 0.2091 gram substance gave 0.2150 gram AgCl.
V. 0.2121 gram substance yielded NH₃ = 14.47 cc. decinormal acid.
VI. 0.2158 gram substance required 14.20 cc. acid.
VII. 0.1930 gram substance required 13.83 cc. acid.
VIII. 0.2648 gram substance gave 0.1633 gram CO₂.

No.	Copper.	Chlorine.	Ammonium.	C₂H₃O₂.
I.	22.00	...	...	...
II.	22.09	...	...	...
III.	...	24.75	...	...
IV.	...	25.35	...	...
V.	...	...	12.34	...
VI.	...	..	11.88(?)	...
VII.	...	...	12.98	...
VIII.	...	...	...	41.35
Average,	22.05	25.05	12.40	41.35

	Calculated for $Cu(NH_4)_2Cl_2(C_2H_3O_2)_2$.	Found.
Cu	22.03	22.05
Cl	24.56	25.05
NH$_4$	12.52	12.40
C$_2$H$_3$O$_2$	40.89	41.35
	100.00	100.85

6. *Tetrammon-Tricupriammonium Bromide*, $3Cu(NH_3)_2Br_2$ $4NH_3$.—Long ago Rammelsberg[1] described two compounds of ammonia and cupric bromide, to one of which, consisting of dark green crystals, he ascribed the formula $CuBr_2.3NH_3$; and to the other, consisting of a bright blue powder, he ascribed the formula $CuBr_2.5NH_3$. Recent investigation[2] has shown that the latter of the two substances must have been in reality $CuBr_2.6NH_3$, which had lost some of its very loosely combined ammonia by exposure to the air. The same investigation brought to light an olive-green substance having the formula $Cu(NH_3)_2Br_2$.

Repeated attempts were made at the same time to obtain Rammelsberg's first substance. The product of these trials invariably consisted of deep indigo, almost black, crystals, which contained noticeably more ammonia than the amount required by Rammelsberg's formula. These deep blue crystals are best obtained by adding, very cautiously, strong hydrobromic acid to a mixture of cupric bromide, alcohol, and just enough *aqua ammonia* to keep all the copper in solution. Upon the addition of enough acid to neutralize the ammonia, the crystals—which are almost insoluble in alcohol—begin to form.

Upon exposure to the air in a moist state these crystals lose ammonia rather rapidly; but when dry they are much more stable. Gentle heat (160°) readily converts them completely into the olive-green $Cu(NH_3)_2Br_2$, which still retains the crystalline form of the more complex salt. It is not impossible that Rammelsberg's green crystals consisted originally of the indigo-colored substance, which had lost superficially a little of its ammonia.

Tetrammon-tricupriammonium bromide is decomposed by water, a noticeable amount of copper going into solution in the form of a soluble compound containing proportionally more ammonia than the original substance. The reaction which takes place may possibly be represented somewhat as follows:

$$Cu_3(NH_3)_{10}Br_6 + 4H_2O =$$
$$[Cu(NH_3)_6Br_2 + 4NH_4Br + Aq] + 2Cu(OH)_2.$$
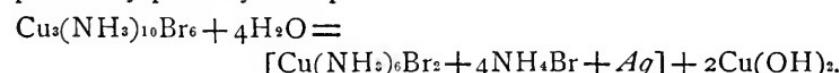
[1] Ann. der Phys. Pogg. **55**, 246.   [2] T. W. Richards: Ber. d. chem. Ges. **23**, 3790.

The amount of water present undoubtedly determines to a large extent the exact nature of the cupriammonium compound which remains undecomposed.

A great number of analyses of the indigo salt were made; partly because of the unusual nature of the formula which they indicated; and partly because the crystals, constantly appearing under many varying conditions in the work which has just been described, needed identification.

Analyses of $Cu_3(NH_3)_{10}Br_6$.

I. 0.4730 gram substance yielded 0.1075 gram Cu.

II. 0.4540 gram substance yielded 0.1033 gram Cu.

III. 0.2614 gram substance yielded 0.0594 gram Cu.

IV. 0.4269 gram substance yielded 0.5721 gram AgBr.

V. 0.4084 gram substance yielded 0 5476 gram AgBr.

VI. 0.2884 gram substance yielded 0.3861 gram AgBr.

VII. 0.1776 gram substance yielded $NH_3 =$ 20.67 cc. decinormal acid.

VIII. 0.1245 gram substance required 14.77 cc. same acid.

IX. 0.1099 gram substance required 12.71 cc. same acid.

X. 0.1288 gram substance required 15.20 cc. same acid.

XI. 0.1175 gram substance required 13.85 cc. same acid.

No.	Copper.	Bromine.	Ammonia.
I.	22.73	...	...
II.	21.75	...	...
III.	22.72	...	...
IV.	...	57.03	...
V.	...	57.06	...
VI.	...	56.97	...
VII.	...	...	19.86
VIII.	...	...	20.25
IX.	...	...	19.74
X.	...	...	20.14
XI.	...	...	20.19
Average,	22.73	57.02	20.06

	Calculated for $CuBr_2.3NH_3$.	Calculated for $(CuBr_2)_3(NH_3)_{10}$.	Found (Mean).
Cu	23.15	22.68	22.73
Br	58.21	57.03	57.02
NH₃	18.64	20.29	20.06
	100.00	100.00	99.81

It is evident that this paper is merely an introduction to the possibilities in the direction indicated. Not only have other compounds of the same acids been already discovered, but many other acids, notably hydriodic, lactic, sulphocyanic, etc., show that they are capable of forming similar compounds. Moreover, the substituted ammonias may apparently take the place of the simple substance in most of the compounds. A few of these preparations are to be seen in the University exhibit at the World's Columbian Exhibition. The study of all these interesting substances will be continued in the immediate future at this Laboratory.

VIII.—THE ACETYL AND BENZOYL DERIVATIVES OF THE PENTOSES.

By W. E. Stone.

Compounds between the better-known sugars (hexoses) and the acetyl and benzoyl radicles have frequently been prepared, and have served to throw light upon the constitution of the former. Theoretically all of the hydroxyl groups of the sugar are supposed to be replaced by the radicles in question, but in practice a complete substitution often fails to be attained. Thus di-, tri-, and tetracetyl compounds of dextrose have been obtained, as well as the pentacetyl dextrose corresponding to the accepted constitution of the latter. The same is true of the other hexoses (galactose and levulose) and of the disaccharides (sucrose, maltose, and lactose). In the same way benzoyl derivatives of the sugars have also been prepared, but these are even less constant in their composition than the corresponding acetyl compounds.

Similar derivatives of the two pentose sugars, arabinose and xylose, have not been prepared, and while the proofs of the constitution of these sugars have been well established by the researches of Kiliani and Fischer, it was still of interest to investigate their behavior in this particular.

Acetyl Derivatives.

Acetyl derivatives of bodies containing hydroxyl groups are as a rule easily formed by Liebermann's method,[1] which consists in heating the water-free substance with acetic anhydride and fused sodium acetate.

Both of the pentoses readily form tetracetyl derivatives corresponding to their accepted constitutions as tetroxy-aldehydes. These compounds have the formula $C_5H_6O_5(CH_3.CO)_4$, and characteristic properties of insolubility, bitter taste and optical activity. No product was obtained containing less than four acetyl radicles.

Tetracetylxylose. — 3 grams of pure xylose $[(a)_D = 18.5°]$ obtained from straw, with 3 grams of freshly fused sodium acetate and 21 cc. of redistilled acetic anhydride, were placed in a flask attached to a reflux-condenser, and heated in a glycerol-bath during one hour at 105° C.

The reaction was attended by slight foaming at 80° to 90°, but was otherwise unmarked. On cooling the mass and adding ice-water in small quantities, there remained a pale-yellow, heavy oil, which after agitation and cooling crystallized as white shining scales. This product weighed upon drying 3.350 grams. It was soluble in warm alcohol, from which it recrystallized with difficulty, and was easily soluble in ether and benzene. It was quite insoluble in cold water, but dissolved easily on warming to 90°, from which solution it recrystallized on cooling in fine needles. The entire amount was recrystallized in this way.

This tetracetylxylose was bitter to the taste; indifferent toward Fehling's solution until after boiling some time, and melted sharply at 123.5°–124.5° without decomposition. A solution in absolute alcohol showed the specific rotation $(a)_D = -25.43°$, without multirotation. Its composition was determined by saponifying and distilling off the free acetic acid. 0.250 gram was placed in a flask, and 50 cc. of water and 25 cc. ½-normal sulphuric acid added. About 50 cc. were distilled off directly, and then the distillation was continued at constant level by means of steam, until the distillate gave no further reaction upon litmus-paper. The distillate was then titrated with ½-normal sodium hydroxide, with the following results:

[1] Ber. d. chem. Ges. **11**, 1619.

	Taken.	Acetic Acid found.	Calculated for $C_5H_6O_5(CH_3CO)_4$.[2]
I.	0.250 gram.	0.1848 gram.	0.1886 gram.
II.	0.250	0.1877	...
III.	0.250	0.1874	...

Tetracetylarabinose.—This was prepared in the same way as described above, but the oily insoluble body remaining after treatment with ice-water refused to crystallize, even when kept at —15° C. for some hours and frequently agitated. It was carefully separated from water and dissolved in absolute alcohol, in which it was easily soluble. This was, after filtration, set aside to evaporate. After drying three weeks over sulphuric acid there remained a dense transparent syrup of pale yellow color. From 3 grams of arabinose, 2.722 grams of this compound resulted. It had the same bitter taste as the xylose derivative; it was insoluble in water, save at high temperature, when it seemed to decompose; it reduced Fehling's solution after heating a short time. A portion was congealed by the use of solid carbon dioxide and ether, and the temperature of the melting mass remained constant at —7.6° for some time. In alcoholic solution it possessed the specific rotation $(a)_D = +26.39$. Upon saponification as already described, the following results were obtained :

	Taken.	Acetic Acid found.	Calculated for $C_5H_6O_5(CH_3CO)_4$.
I.	0.2773 gram.	0.2018 gram.	0.2091 gram.
II.	0.1489	0.1074	0.1121
III.	0.3298	0.2402	0.2489

These numbers conform less closely to the theoretical than those for the xylose derivative, but it was hardly possible to bring the arabinose compound to a high degree of purity. Both were undoubtedly tetracetyl derivatives. That their specific rotations were practically equal, but in opposite directions, was at least a noticeable coincidence.

Benzoyl Derivatives.

According to the method proposed by Baumann,[1] benzoyl chloride reacts upon the sugars, forming benzoyl esters in which the hydrogen atom of each hydroxyl group of the sugar is replaced by the benzoyl radicle.

Baumann's method has been somewhat modified by Panormoff,[2] but it seems to be the common experience that the theoretical

[1] Ber. d. chem. Ges. **19**, 3220. [2] Chem. Centralb. 1891, **2**, 853.

reaction does not always occur. At least the derivatives thus obtained from the sugars are of variable composition, and Ruenz[1] intimates that such products are not single compounds, but mixtures of more or less complete esters.

To 1 part of xylose dissolved in water were added 160 parts of 10-per cent. sodium hydroxide solution and 18 parts of benzoyl chloride, and the whole thoroughly shaken together for a quarter-hour. A foamy substance gradually formed on the surface of the liquid, which upon standing became firm and tenacious, and on cooling was brittle. Arabinose treated in the same way yielded a similar product. Both preparations were washed with warm water and dissolved with hot alcohol, from which they were again precipitated by water. They were again redissolved in hot alcohol, and left to crystallize by slow evaporation. The xylose derivative crystallized slowly in large pointed crystals. The arabinose compound separated more rapidly as oily colorless drops which refused to crystallize. It was redissolved in hot alcohol, and, by addition of pieces of ice, was thrown down as an amorphous flocculent precipitate.

Both products were entirely odorless and tasteless. They were without effect upon boiling Fehling's solution. The benzoyl-xylose melted at $164°–165°$; the arabinose derivative at $68°–69°$; both were free from ash and chlorine. Analyses, however, failed to give any numbers corresponding to the calculated values for any single benzoyl derivative of a pentose. They were undoubtedly mixtures of different compounds.

The above results show that these pentoses behave like the other sugars in this respect, as has already been proved in regard to other reactions, while the introduction of four acetyl groups sustains the constitution already assigned them as tetroxyaldehydes.

IX.—THE ELECTROLYTIC OXIDATION OF GLYCEROL.

By W. E. Stone and H. N. McCoy.

The action of an electric current upon dilute solutions of glycerol has been studied by Rénard,[2] who noted formic, acetic, oxalic, and glyceric acids as well as simple and polymeric trioxy-

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[1] Ztschr. physiol. Chem. **14**, 330.   [2] Ann. chim. Phys. [5], **17**, 303.

methylene as products when the electrolyzed solution was acidulated with sulphuric acid. Bartoli and Paspagoli[1] observed under the same conditions, acroleïn, formic and glyceric acids, and trioxymethylene.

Lately E. Fischer[2] has shown that glycerol is oxidized to glyceral by the action of bromine, and with the glyceral thus obtained he accomplished the synthesis of glucose. We have attempted a similar partial oxidation of glycerol by the action of weak electric currents upon dilute solutions, and have succeeded in obtaining in this way small quantities of glyceral, but in general the action of even a weak current seems to accomplish complete oxidation of the alcohol in question, so that glyceral is only a transitory and intermediate product of the operation and ordinarily would elude observation.

We have studied the subject under varying conditions, the results of which will be summarized here. The apparatus employed was simple, consisting of one or two large bichromate-cells connected with electrodes of platinum, of an area of about $1\frac{1}{2}$ square inches, which were submerged in the solutions to be studied. The strength of the current was measured by a Bunsen voltameter and was always less than 0.3 ampère. As glycerol is a nonconductor of electricity, it was necessary to add to the solution some conductor, which at the same time served to render the solution respectively acid, alkaline, or neutral, in reaction, and this in turn was found to have a decided influence upon the character of the products obtained. The solutions were usually made up of 20–25 grams of glycerol diluted to 200 cc. with water.

Oxidation of an Acid Solution.—A 10-per cent. solution of glycerol slightly acidulated with sulphuric acid and subjected to the action of a current of 0.2–0.3 ampère shows a rise in temperature, presently becomes able to produce a strong reduction of Fehling's solution *in the cold*, and to give the ordinary fuchsin-reaction for aldehydes. Later a perceptible odor of acroleïn is observed. The strong reduction of Fehling's solution in the cold is characteristic of glyceral. Eventually more or less of the glycerol becomes converted into acids, according to the duration of the action, but at no time was it possible to isolate any glyceral.

Oxidation in a Neutral Solution.—As a conductor 0.2 gram of sodium nitrate was used in 200 cc. of a 10-per cent. glycerol solu-

[1] Gaz. chim. Ital. **13**, 287.   [2] Ber. d. chem. Ges. **20**, 3385.

tion. An acid reaction is soon noticeable—due to the formation of acids from the glycerol—and from this point the results were like those when free sulphuric acid was present; the solution gives a strong reduction with Fehling's solution in the cold, gives the fuchsin-reaction and smells of acroleïn.

Oxidation in an Alkaline Solution.—A small quantity of sodium hydroxide was added to a 10-per cent. solution of glycerol, which was then electrolyzed as above. The first visible result was the appearance of a yellow color in the solution, which after some hours disappeared and then it was found that the solution was acid in reaction. In another trial 5 per cent. of sodium hydroxide was used and the yellowish brown color was very noticeable, but disappeared upon subsequent acidulation with acetic acid. Several oxidations were made in which a known amount of alkali and a known amount of glycerol were employed, and by subsequent titration it was found in all cases that a large amount of acid had been formed. In one case the acid amounted to 80 per cent. of the glycerol employed. These solutions also had the property of reducing Fehling's solution in the cold, but no odor of acroleïn was perceptible.

The conclusions drawn from these general experiments were that glycerol is very susceptible to the action of electrolytic oxygen; that, first, a body with the property of an aldehyde is formed and is at once farther oxidized to an acid. The noticeable yellow color in the electrolyzed alkaline solution seemed explainable by the fact, as shown by Fischer, that glyceral, $C_3H_6O_3$, is easily polymerized in the presence of an alkali to glycerose (or glucose), $C_6H_{12}O_6$, and it is well known that the latter in contact with alkalies takes on a yellow color. In the above case it would seem that the glyceral, as formed, was polymerized to glycerose. This suggested a means of removing the glyceral from farther oxidation.

A weak current of less than 0.1 ampère was passed through an 8-per cent. solution of glycerol to which 0.5 per cent. of sodium hydroxide had been added, for a period of six days. The electrolytic cell and contents were kept cool (20° C.) by running water. The alkali was renewed once. A yellow color soon appeared in the solution and a strong reduction of Fehling's solution was produced in the cold. The filtrate from such a test, which gave no farther reaction in the cold, reduced still more strongly on boiling,

indicating a partial polymerization of the aldehyde. At the expiration of six days the current was interrupted, 2 per cent. more sodium hydroxide added and the whole placed in the cold during four days. The yellow color in the meantime became intensified, but the power to reduce Fehling's solution in the cold disappeared entirely, while the reduction on boiling was markedly increased. All of this pointed to the formation and polymerization of glyceral. In order to prove the presence of this polymeric product, glycerose, resort was had to the characteristic phenylhydrazine compound and to the fermentation-test. The alkaline solution was carefully neutralized and one-half was treated with phenylhydrazine chloride and sodium acetate in the usual way. The solution, after heating in boiling water for six hours, on cooling threw down a voluminous golden yellow precipitate. This, after repeated recrystallization from benzene and ethyl acetate, melted at 200° C. The quantity did not admit of further purification. The melting-point of glycerosazone was found by Fischer to be 204°.

The second portion of the solution above described was placed in contact with fresh brewers' yeast alongside of a blank containing only yeast and water. A lively fermentation began at once in the electrolyzed solution and continued normally until 25–30 cc. of carbon dioxide gas had been collected. No fermentation occurred in the blank sample. This result as well as the character of the phenylhydrazine derivative leaves no doubt as to the formation of an appreciable quantity of glyceral by the action of a weak current upon an alkaline solution of glycerol under such conditions as to facilitate polymerization of the former.

Glyceric Acid and its Optically Active Modification.

Glyceric acid, $C_3H_6O_4$, results as one of the products of the electrolytic oxidation of glycerol. It may be prepared more readily, however, by the oxidation of glycerol by nitric acid.[1] A more recent method suggested by Börnstern,[2] involving the action of mercuric oxide upon glycerol in alkaline solution, is easy to carry out and yields a product of high purity. As prepared by any of these methods, glyceric acid is optically inactive, although it contains an asymmetric carbon atom, and according to the theory at present accepted should be optically active. Its inactivity is,

[1] Mulder: Ber. d. chem. Ges. 3, 1902.   [2] *Ibid.* 18, 3357.

however, explained on the assumption that it consists of equal or compensating portions of active acids respectively dextro- and laevo-rotatory. Such has been shown to be the fact in the cases of the inactive racemic, malic, lactic, asparagic, mannonic, galactonic and other acids, the separation of which into their optically-active isomers has been accomplished in different ways. Indeed, by the fermentative action of certain organisms there have been obtained from glyceric acid both the dextro- and laevo-rotatory modifications. Lewkowitch,[1] by cultivating *Penicillium glaucum* upon neutral inactive ammonium glycerate obtained laevo-glyceric acid, while Frankland and Frew, by a similar decomposition of neutral inactive calcium glycerate, obtained dextro-glyceric acid.[2] A complete separation and identification of both the active forms from a single portion of the inactive glyceric acid has, however, not yet been accomplished, although several other of the inactive acids have been separated in this manner. We have attempted this operation with glyceric acid, studying its salts with the alkaline earths and with certain alkaloids, but thus far without success. Strychnine and cinchonine glycerates were prepared and subjected to fractional crystallization, but in no case after decomposing the fractions was the free acid active. In the same way fractional solution in a variety of solvents was employed, but also without positive result. It appears that the separation of this acid into its optical isomers presents greater difficulties than some others which have been thus resolved.

X.—THE CARBOHYDRATES OF THE FRUIT OF THE KENTUCKY COFFEE-NUT TREE (*GYMNO-CLADUS CANADENSIS*).

By W. E. Stone and W. H. Test.

This tree, which occurs in fertile soils in the west and southwest of the United States, is closely related to the common thorny or honey locust (*Gleditschia*) and the European *Ceratonia siliqua*, the fruits of both of which are edible. The fruit of *Gymnocladus* resembles the others somewhat in appearance. It consists of a leathery pod of from three to ten inches in length, containing from two to six brown, oval and very hard seeds. These seeds are

[1] Ber. d. chem. Ges. **16**, 2720.   [2] Trans. Chem. Soc. 1891, 96.

imbedded in a greenish waxy pulp or gum which possesses a sweet but also very disagreeable taste. This gum at the time of ripening is soft and easily removed, but later becomes hard and horny.

On account of the relation between this tree and those species producing the valuable commercial gums (gum arabic, gum copal, etc.), it was thought that this material (the gum) would repay investigation. Some preliminary tests showed the presence of an abundance of soluble reducing sugar and of pentosans (17 per cent.). The absence of galactose or galactan and of starch was also proven.

Forty of the seed-pods, collected in October, yielded 1300 grams of the fresh gum, which contained 52 per cent. of the moisture, leaving 675 grams of dry solid matter. This gum was extracted with 2500 cc. of boiling alcohol of 78-per cent. strength during six hours. This was filtered off and a second extraction made with 2000 cc. of alcohol of the same strength, also during a period of six hours.

In this way the sugars were dissolved and were removed by washing the insoluble gums on a filter until the washings gave no further reaction for sugar with Fehling's solution. The alcoholic extracts and the insoluble residue were examined separately.

The alcoholic extract was evaporated to a syrup and the impurities removed by the use of bone-black, precipitation with strong, hot alcohol, etc. Finally upon addition of a large volume of strong alcohol, a crop of fine white crystals was obtained, amounting to 20 grams in weight. These crystals consisted of a sugar, soluble in water, sweet, without direct effect upon Fehling's solution, but reducing strongly after inversion, and with a specific rotation $(\alpha)_D = 65.4°$, which after inversion became slightly laevo-rotatory. This sugar was therefore sucrose, of which, by continued crystallization, fully 100 grams were obtained. Taking into account the amount not recovered from the mother-liquor, this sucrose amounted to about 15 per cent. of the dry matter of the gum. There remained a large amount of uncrystallizable syrup, weighing about 130 grams, which contained a quantity of reducing sugar. From this a phenylhydrazine compound was prepared which melted at 203°, indicating glucose. The dry matter of the gum as taken from the seed-pod contained therefore about 15 per cent. of sucrose and an almost equal amount of glucose.

The gummy residue remaining after the soluble sugars had been extracted as above described was hydrolyzed by the action of 4000 cc. of 2-per cent. sulphuric acid at the temperature of boiling water during 12 hours. A portion of the material was dissolved, and a portion resembling cellulose remained behind. After filtration the solution was neutralized by calcium carbonate and concentrated by evaporation. After repeated attempts at purification there remained a thick, sweet syrup, which reduced Fehling's solution strongly, but refused to crystallize even on long standing. The furfurol-reaction revealed the presence of one of the pentoses. A phenylhydrazine compound melted at 175°–180°, which indicated a mixture of two or more sugars. A small portion of this compound was treated with just sufficient 95-per cent. alcohol to dissolve it at the boiling temperature; on cooling, a mass of fine yellow crystals separated, which melted sharply at 204°–205°, corresponding to the glucose derivative. On adding water to the filtrate, a yellow, flocculent mass was precipitated which melted at 140°–150°. This suggested a means of separating the phenylhydrazine compounds of the two sugars, which were evidently both present, by means of their different solubilities in water. Phenylxylosazon was found by actual experiment to be soluble in about 50 parts of boiling water, from which it separates on cooling. Phenylglucosazon, on the other hand, is quite insoluble in boiling water. The entire amount of the syrup was now converted into the phenylhydrazine compound, which weighed about 25 grams. A small portion of this, treated with 95-per cent. alcohol as already described, yielded a product melting at 204°–205° and containing no trace of a pentose, as shown by the furfurol-reaction. The larger portion of the mixture was boiled with 50 parts of water for two hours, upon which a considerable portion went into solution, was filtered off, and precipitated again on cooling. This was again recrystallized from hot water. The product thus obtained melted at 153° and gave an abundance of furfurol on heating with strong hydrochloric acid (the melting-points of both arabinosazon and xylosazon are 158°–160°). This may be taken as satisfactory proof of the presence of one of the pentoses. Its alcoholic solution was optically inactive, which distinguishes it from xylosazon, which has been shown to be active.

The insoluble gum of the fruit yielded, therefore, upon inversion, two sugars of distinctly different classes, a pentose (probably

arabinose) and a hexose (dextrose). It still remains a question if these were derived from separate mother-substances in the gum or from a single homogeneous substance, to which the name gluco-araban may be given, corresponding in its nature to the pentosans, galactan, etc. Such substances have been but sparingly noted. The first instance of the kind was recorded by one of us in the gum exuded from the bark and fruit of the peach-tree, which yields, on inversion, galactose and arabinose.[1] A similar galacto-araban has been noted in the coffee-bean[2] and in the seeds of certain leguminosae,[3] and a xylo-araban in the bran of wheat and rye.[3] This seems to be the first recorded observation of a gluco-araban.

In conclusion, the carbohydrates of the fruit of *Gymnocladus* seem to be remarkable in variety and abundance. Sucrose and glucose are both present in large quantities, while the insoluble portion contains bodies or a body which, on inversion, yields a pentose and glucose, to which the name of gluco-araban may be provisionally applied.

THE ACTION OF SALTS ON ACIDS.

By R. W. Wood.

In Volume VIII, Number 3, of this Journal there appeared an article by J. R. Duggan, "On the determination of absolute neutrality." The author used diastase and starch as an indicator of neutrality, the presence of a small trace of acid or alkali inhibiting the action of the ferment. He found that in the case of weak acids a small amount of their neutral sodium salts prevented their inhibiting action on diastase, and in consequence he came to the conclusion that the salts must be alkaline. In the case of sodium acetate he found that 0.06 gram (2 equivalents) of acetic acid could be added to the starch in the presence of 0.02 gram (1 equivalent) of sodium hydrate, without affecting the diastase, while half this

[1] This Journal **12**, 435.   [2] E. E. Elwell: This Journal **14**, 473.
.Schulze: Chem. Centralbl. 1892, **1**, 701.

amount of acid in the starch, no salt being present, would practically prevent all action of the ferment.

Sodium acetate he considered an alkaline salt, requiring the addition of another equivalent of acid to make it absolutely neutral. Such a solution is, however, strongly acid to other indicators, and the mere fact that its action on diastase is not inhibitory may not justify one in calling it neutral.

Duggan's work was done with great care; he examined various acids and salts and obtained interesting results, but there were several points that he overlooked in his investigations, which seem to show without question that some, at least, of the conclusions that he drew were erroneous.

The modern theory of dissociation seems to offer a better explanation of the phenomena, for the results of experiments seem to bear out the hypothesis that the inhibiting action on diastase is due to the free ions of hydrogen in the case of acids, and of hydroxyl in the case of alkalies. In the case of salts of weak acids it seems probable that part of the salt takes up water and dissociates into acid and base, the latter then being more fully dissociated into its ions, and the solution therefore acting like a base; on now adding an excess of acid this is dissociated, but not to the same extent as if no salt were present. When as many hydrogen ions as hydroxyl are formed in unit time, the solution no longer reacts on the diastase and we have what Duggan called absolute neutrality. The addition of more acid brings about action, though here again the restraining influence of the salt is felt.

When working under exactly the same conditions, the actions of salts and acids in varying proportion on diastase are so uniform that it seems highly probable that the method can be used for determining the amount of hydrolytic dissociation that occurs in salt solutions. The results given in this paper are not as accurate as it would be possible to obtain with specially constructed apparatus, for in certain cases very slight changes of temperature cause very wide variations. The work thus far has been essentially preliminary, there being many difficulties to overcome. Better results are expected in the continuation of the work with apparatus adapted to it. Duggan's work has been repeated, and enlarged upon to some extent, and the results seem to put the subject in a different light.

Materials and Methods.

The diastase was prepared by macerating finely ground pale barley-malt in distilled water for three hours, at the temperature of the room : the mush was squeezed in cloth bags, the fluid filtered to remove starch grains, and the diastase precipitated from the clear yellow solution by the addition of twice its volume of 95-per cent. alcohol. The precipitate was washed with absolute alcohol, dried in a vacuum over sulphuric acid, and very finely ground in an agate mortar. The product had a light brown color and was very energetic, converting about 75 times its weight of starch into maltose at 55° C. in thirty minutes. Duggan does not state how his diastase was prepared or how active it was. In his preliminary work he used commercial malt-extract, which is unsatisfactory. The starch was Taylor's preparation of Bermuda arrow-root, which was the purest that could be conveniently obtained.

2 grams of starch was found to be the best amount for each determination. It was stirred up in 5 cc. of water, and then added to 75 cc. of boiling water, forming a thin paste. The diastase was weighed each time to within 0.1 mg., 0.01 gram being the amount taken. It was stirred up with 10 cc. of water in a beaker, and put into a double-walled air-bath heated to 55° by boiling acetone. When the starch-paste had cooled down to about 60°, the acid or alkali or both were added by means of a graduated pipette, and when the temperature had fallen to exactly 55°, the paste was quickly poured into the beaker containing the diastase, and the air-bath quickly closed. The paste was stirred twice, once at the end of ten minutes, again at the end of twenty minutes, and at the expiration of thirty minutes the action was stopped by the addition of 2 cc. of a 10-per cent. solution of sodium hydroxide. The solution was then made up to 100 cc., and the sugar that had been formed determined volumetrically by Fehling's solution and reported as maltose.

Action of Acids and Alkalies on Diastase.

The action of sodium hydroxide was first tried, the determinations being made in a special room where the absence of fumes from the air could be assured. The alkali solution contained 0.8 gram of the base per liter. 1 cc. of this solution in 80 cc. starch-paste would correspond to ten parts of the alkali to one million of paste. The solution was made of this strength in order that the

results obtained might be compared with the results obtained by Duggan in his preliminary work. The following table indicates the action of varying amounts of alkali on 2 grams of starch and 0.01 gram diastase:

cc. of NaOH sol.	0	0.1	0.2	0.3	0.4
Parts to million	0	1	2	3	4 .
Maltose	0.739	0.674	0.639	0.616	0.508

cc. of NaOH sol.	0.5	1	1.5	2
Parts to million	5	10	15	20
Maltose	0.454	0.235	0.107	0.077

This table shows that the diastase was much more sensitive than that used by Duggan : the smallest proportion of alkali that he detected was five parts to the million, whereas in this case one part gave a very perceptible retardation. A solution of phenolphthaleïn showed no trace of color until six parts of sodium hydroxide to a million of water were present. This shows how sensitive a substance diastase is. No other alkalies were tried.

The acids investigated were of the fatty series, and the solutions were all made equivalent to the alkali solution, by careful titration with phenolphthaleïn. Acetic acid gave the following results :

Acid, in cc.	0	0.5	0.75	1	1.5	2
Maltose, in grams	0.739	0.800	0.874	0.855	0.820	0.785

Acid, in cc.	3	4	5	7.5	10	20
Maltose, in grams	0.636	0.481	0.320	0.248	0.197	0.128

This series shows, what Duggan and others have found to be true, that a slight amount of acid has a favoring action, due probably to some impurity in the starch which, alone, exerts an inhibiting action, but is destroyed or neutralized by a small amount of acid. The effect of the acid is much less than that of an equivalent amount of alkali. Monochloracetic acid gave the following results:

Acid, in cc.	0.3	0.5	0.7	1
Maltose, in grams	0.785	0.874	0.835	0.810

Acid, in cc.	1.2	1.5	2
Maltose, in grams	0.639	0.359	0.185

which show that up to the point where the impurity in the starch is neutralized the stronger acid acts much like the weaker, but

when this point is passed, exerts a much more powerful action on the diastase. This was found to be true with all the acids tried, and seems to indicate that the impurity in the starch has the properties of an alkali and is neutralized by a certain definite equivalent of acid, wholly independent of the affinity of the acid. The action on the diastase depends on the nature of the acid as well as on the actual quantity. Dichloracetic and trichloracetic acids were tried, but did not give concordant results ; the reason for this was subequently ascertained and will be referred to later. The other fatty acids retarded as follows :

Formic, in cc.	1	1.5	2
Maltose, in grams	0.547	0.296	0.173
Propionic	3	5	10
Maltose	0.592	0.320	0.184
Butyric	2	5	10
Maltose	0.854	0.320	0.128
Valeric	5	10	
Maltose	0.349	0.120	

These results are only *approximate*. It was found very diffi-cult to get concordant results with any of the stronger acids. In the case of dichloracetic and trichloracetic acids this was at first thought to be due to the decomposition of the acids in solution, but as the same errors were found with perfectly stable acids, it seems probable that slight variations of temperature were respon-sible for the discrepancies. One determination with formic acid had given a yield of 0.290 gram maltose; a second gave 0.460 gram with the *same* amount of acid. It was thought that prob-ably the small yield was due to the fact that the temperature was a little too low. Two determinations were made, taking scrupu-lous care to have the temperature exactly 55° (the most favorable one for diastatic action), and the yield in each case was 0.290 gram : *the smaller yield*. A determination was then made at 45° and the yield was found to be nearly 0.500 gram, showing that in the presence of an acid the most favorable temperature is much lower than when the acid is not present, or, in other words, that the power of the acid increases with the temperature to a much greater extent than the power of the diastase. With other acids the following effects were observed :

Acetic	Temp.	Maltose	Butyric	Temp.	Maltose
5 cc.	55°	0.305	10	55°	0.128
5	45°	0.470	10	45°	0.240

Valeric	Temp.	Maltose
5	55°	0.349
5	45°	0.577

This may be used for the determination of the effects of temperature on the action of the acids, and will be investigated later on. Very slight variations in temperature will produce very large variations in the results, and for this reason I do not attach much importance to the figures obtained with acids alone, since owing to the nature of the materials and apparatus it was difficult to be sure of the temperature within two degrees. The paste is with difficulty brought to a uniform temperature throughout, owing to its viscosity, and in pouring it suffers considerable loss of heat. The work is to be continued with a piece of apparatus designed for the purpose, in which six determinations can be made simultaneously, thereby ensuring similar conditions. The six beakers of starch are emptied into the six glasses containing the diastase by a mechanism operated from the outside of the closed chamber in which they are heated. Stirring-rods are kept in constant motion by a water-motor and the temperature can be kept constant within a quarter of a degree or less. The other results given in this paper may be considered fairly accurate, since very small variations in temperature, except in the presence of strong acid, seem to produce but little effect.

Action of Salts on their Acids.

It is from the results obtained in studying the action of salts on their acids that the most interesting theoretical deductions are to be drawn. Neutral salts of the weak acids above mentioned have a slight retarding effect, and in general the weaker the acid the greater the inhibiting action of its salt. Salts of strong acids, such as sodium chloride, have little or no effect on diastase.

Equivalent amounts of salt were used each time, *i. e.*, the quantity formed from 0.04 gram sodium hydroxide. In the case of sodium acetate this would give 0.082 gram of salt. In all the following cases 0.04 gram alkali is the amount used, and the retardation with one equivalent of acid is of course the retardation due to the neutral salt. The quantities of acid are given in equivalents:

Acetic,	1	$1\frac{1}{6}$	2	$2\frac{1}{2}$	3	5	
Maltose,	0.662	0.874	0.874	0.874	0.8	0.4	
Formic,	1	$1\frac{1}{16}$	$1\frac{1}{10}$	$1\frac{1}{5}$	$1\frac{2}{5}$	$1\frac{4}{5}$	
Maltose,	0.6	0.874	0.874	0.8	0.385	0.115	
Propionic,	2	3	4	5	6	8	10
Maltose,	0.874	0.874	0.874	0.828	0.55	0.4	0.16
Butyric,	1	$2\frac{2}{10}$	$2\frac{1}{2}$	3	4	6	
Maltose,	0.481	0.874	0.74	0.693	0.427	0.18	
Valeric,	1		3		4		
Maltose,	0.481		0.662		0.427		

It seems best to postpone a discussion of these figures with their theoretical bearing until fuller and more accurate results are obtained. It did not seem best to attempt with comparatively crude apparatus to make out very complete tables, since the object of the investigation thus far has been to obtain a general idea of the nature of the actions, rather than exact numerical results. In the case of the acetate, $\frac{1}{6}$ of an equivalent of acid in the presence of the salt gives the maximum yield of sugar, or the yield that is given when the impurity in the starch has been neutralized. Above this point we may continue to add acid until there are nearly two equivalents in excess, and still get the maximum yield. Then the acid begins to retard, but not nearly in the degree that it would if no salt were present. It may be that as soon as there is present a sufficient quantity of acid to give the maximum yield, a further addition will cause instant retardation, but it is so slight that it is impossible to detect it. The other acids behave in general in the same way; the retardation with formic commencing when $\frac{1}{5}$ of an equivalent is in excess, while propionic gives no sign of retarding action until four equivalents are in excess. It will be seen that the maximum yield is given within quite a large range (though this is probably due to lack of delicacy of the indicator), hence it is not strange that Duggan came to the erroneous conclusion that absolute neutrality was obtained by the addition of exact equivalents of acid in excess.[1]

[1] Since this paper has been put in type an article has appeared (Ztschr. phys. Chem. 12, 167) by Shields, who has been working with Arrhenius on this same problem. His method is wholly different from the one described in this paper, depending on the power of hydroxyl to saponify ethyl acetate. It will be interesting to see how future numerical results compare with the results obtained by him.

In conclusion I wish to make acknowledgment to Dr. Felix Lengfeld, at whose suggestion this work was undertaken, for the many suggestions, both practical and theoretical, that he has given me,

REVIEWS AND REPORTS.

RECENT PROGRESS IN PHYSICAL CHEMISTRY.—IV.

The Energy-Theory.

We learn from experience that heat, work, electricity, and the like are mutually convertible. They are therefore the same kind of thing, and this kind of thing has received the general name Energy.

The work of J. R. Meyer and of Helmholtz, a half-century ago, in straightforwardly stating the significance and bearing of the energy-conception, marked the dawning of a new era in the rational development of the physical sciences. A recognition of the great fact that energy is the actuality with which exact science has to deal is making it possible to pass from the more purely descriptive stages of scientific work to a systematic study of causal relations; to build upon this conception of energy a strict and coherent theory of phenomena.

In no department of science are the results already reached so full of promise as they are in chemistry. The mutual relations of heat, electricity, volume-energy, and the like in determining the character of chemical processes and the state of chemical systems are now clearly seen to be of fundamental importance. Chemists have waited long for this insight. It has been delayed by the obstinate and crude idea that all forms of energy are forms of mechanical energy, and that in consequence mechanical hypotheses are necessary for the explanation of natural phenomena. This belief arose, after the discovery of the mutual convertibility of heat and work, from the simple fact that the mechanical energies were the best known. For the old method is substituted a web of exact relations between the energy-phenomena coming in question. Physical theory and not mechanical hypothesis has become the guiding-star.

The energy-method, now coming to full fruition, has not been totally neglected in these intervening years, as is evinced by the

discoveries of Kirchhoff concerning solutions, by those of Helm-holtz in electro-chemistry and chemical affinity, by the Intensity Law of Helm, and by the remarkable and yet too little understood theoretical work of our own countryman, Willard Gibbs.[1]

The different sciences would be wholly distinct were the several energy-forms which they treat not mutually convertible. This convertibility, and this alone, unites them into a general Science of Energetics. By using energy, space and time as the units common to them all,[2] there are obtained throughout measurable relations between them. The subjects of chemistry, electricity, heat and work are thus brought together, and the respective transformations of the energies involved furnish the subject-matter of the sciences of electro-chemistry, thermo-chemistry, electro-dynamics, thermodynamics and mechanics.

In a paper subsequent to the one cited, Ostwald directs especial attention[3] to the resolution of the analytical expressions of the various energy-forms into their factors, one of which has the character of an *intensity* of the energy-form in question, and the other that of a *capacity* for it. The intensity-factor determines whether its energy may or may not be at rest, having, by definition, the same value for two energy-quantities which do not influence each other. Examples of this resolution into factors are:

		Capacity.		Intensity.	Formula.
Mechanical energies.	Distance-energy	= distance	×force		$s \cdot f$
	Surface-energy	= surface	×tension		$O \cdot \gamma$
	Volume-energy	= volume	×pressure		$v \cdot p$
	Motion-energy	= mass	×velocity square		$\frac{1}{2}m \cdot V^2$
Other energies.	Electricity	= quantity	×potential		$\varepsilon \cdot \pi$
	Heat	$= \dfrac{dQ}{dT}$ or $\left(\dfrac{Q}{T}\right)_T$	×temperature		$\dfrac{Q}{T} \cdot T$
	Magnetism	= mag. quan.	×mag. potential		$e \cdot ll$

The observed impossibility of creating energy from nothing, of creating the ultimate reality, is formulated as the First Law of Energetics: The energy of the universe is constant. A similar recognition of the impossibility of unlimited transformation of one energy-form into another without intensity-differences, as in obtaining work from a quantity of heat of uniform temperature or from electricity of uniform potential, constitutes the Second Law of Energetics: Unlimited conversion of an energy, without intensity-differences, is impossible.

The condition for the equilibrium of a single energy-form—that its intensity shall be uniform throughout—is, in its application, very familiar. The heat in a bar of iron, which is hot at one end,

[1] Trans. Conn. Acad. **3**; Thermodynamische Studien (translated by Ostwald), Leipzig, 1892.
[2] Ostwald: Ztschr. phys. Chem. **9**, 563 (1892).
[3] Ztschr. phys. Chem. **10**, 363 (1892).

will be transferred by conduction until the temperature-differences shall have become equalized ; a mass of a gas must have uniform pressure throughout (the effect of gravitational energy supposed eliminated) ; electricity will not pass from one electrically charged body to another when both quantities of electricity have the same potential ; two moving masses will not influence each other's motion if their velocities be the same (they must correspondingly have the same direction of motion, for the definition of a velocity includes a direction). The same rule applies to the other energy-forms.

But that feature of the energy-theory which is of the most especial interest at the present time, is its treatment of the equilibria between several energy-forms which oppose one another in the same system. Such an equilibrium is said to obtain when no transformation of one energy-form into another takes place. The equilibrium eventually reached may be disturbed by a change of the intensity-factor of any one of the energies involved, this causing an opposed change of the correlative energy-forms. At equilibrium, an infinitesimal change (virtual change) of one of the energies must be exactly balanced by the resulting virtual changes of the others.

The necessary and sufficient *condition of equilibrium*, then, for any material system whatsoever, is :

The algebraic sum of the energy-changes involved in a virtual displacement of the equilibrium must equal zero.[1]

If energy, capacity and intensity be represented by E, C and I, respectively, this condition is expressed analytically by

$$\Sigma \delta E = 0 \quad \text{or} \quad \Sigma C.dI = 0,$$

the summation being taken over all the correlated energies of the system. It is known as the Principle of Virtual Energies, and it represents the theory of all equilibria whatever, whether they be those of statics, of thermodynamics, of chemistry, or of any other branch of general energetics. This is the most important element of Ostwald's work in the energy-theory.

Systematic application of this principle of virtual energies has shown strikingly the analogy in character between various important and apparently heterogeneous relations.

The amount of work gained in the isothermal expansion of a dissolved substance, or of a gas, from a given initial pressure P to a lesser one p is

$$\int dW = -\int_P^p v\,dp$$
$$= -RT \int_P^p \frac{dP}{P},$$
$$W = RT \log \frac{P}{p},$$

[1] Ostwald, l. c. 1892.

the integration being effected with the aid of the equation of condition of dilute matter, $pv = RT$. The resulting equation, giving the work-value of a concentration-change in a dilute solution (van't Hoff, 1887), or in a voltaic cell (Nernst, 1889), is a fundamental one in the theory of solutions and in electro-chemistry.

Other differential equations of the same form $\Sigma Cdl = 0$, but not integrable in this way, express the mutual dependence of (1) electricity, (2) surface-energy, (3) heat, (4) volume-energy. Arranged in order, they are—

For the equilibrium between electricity and surface-energy:

$$Od\gamma = -\varepsilon d\pi,$$
$$\frac{d\gamma}{d\pi} = \frac{-\varepsilon}{O},$$

the relation between surface-tension and electromotive force.

That between surface-energy and heat:

$$\frac{q}{T} \cdot dT = O \cdot d\gamma,$$
$$\frac{d\gamma}{dT} = \frac{q}{T \cdot O},$$

an expression for the temperature-coefficient of surface-tension.

That between electricity and heat:

$$\varepsilon d\pi = \frac{q}{T} \cdot dT,$$
$$\frac{d\pi}{dT} = \frac{q}{T \cdot \varepsilon},$$

the famous equation of Gibbs and Helmholtz, introducing the element of temperature into the theory of electro-chemistry.

That between heat and volume-energy $[(v' - v) =$ increase of molecular volume caused by the change considered],

$$\frac{q}{T} dt = (v' - v) dp,$$
$$\frac{dp}{dt} = \frac{q}{T(v' - v)},$$

a relation comprehending the extremely extended theory of such changes of state as are involved in the processes of vaporization, sublimation, dissolving, melting and the transformation of allotropic forms. It is familiarly known as the Clausius vaporization-formula.

All these special cases of the equation are of the form

$$c' \cdot dl' = c \cdot dl$$

or

$$\frac{dl'}{dl} = \frac{c}{c'},$$

and they express the details of what is known as the Theory of the "Complete" Chemical Equilibria.

In a paper read at the World's Congress at Chicago, the writer has pointed out the bearing of the energy-theory in expressing the influence of extraneous energy-forms upon the purely chemical volume-energy equilibria of reversible reactions. When a system of reacting substances is in equilibrium, the total virtual change $\Sigma v d p$ of the volume-energy of the reaction-products is balanced by that $\Sigma V d P$ of the original substances. p and v represent throughout the partial pressures and reacting volumes of the substances in question, and when the system is left to itself, the fundamental equation (3) assumes the form

$$\Sigma v d p - \Sigma V d P = 0.$$

With the aid of the general "equation of condition" of dilute matter, $pv = nRT$, whence $p = nRTv^{-1}$ and $dp = -nRT\frac{dv}{v^2}$, we can eliminate the pressure-factor, obtaining

$$- RT (n\Sigma d \log v - \Sigma d \log V) = 0,$$

whence, at constant temperature, replacing the molecular volume by its reciprocal, the molecular concentration,

$$\Sigma \partial \log c^n = \Sigma \partial \log C^N.$$

The integral of this equation furnishes the concentration-relations for a chemical equilibrium at constant temperature,

$$\Sigma \log c^n + \log k' = \Sigma \log C^N + \log k,$$

i. e.
$$\frac{c_1^{n_1}.c_2^{n_2}\ldots}{C_1^{N_1}.C_2^{N_2}\ldots} = \frac{k}{k'} = K,$$

or
$$c_1^{n_1}.c_2^{n_2}\ldots = K.C_1^{N_1}.C_2^{N_2}\ldots,$$

which states the effect of each reacting substance to be proportional to its concentration ; K is the "equilibrium-constant." This is the famous Law of Mass-Action, expressing the conditions of chemical equilibrium at constant temperature.

Further, if pressure be applied to a system of reacting substances, work is done upon the system and a deformation of its chemical equilibrium results. The principle of virtual energies represents this equilibrium between volume-energy and work in the form

$$- \Delta v . dp - (\Sigma v d p - \Sigma V d P) = 0,$$

where $-\Delta v$ is the volume-decrease accompanying the reaction in question, and is a function of the molecular volumes of the substances. The bracketed expression has been already found to be $RT\partial \log K$, K being at a given temperature the constant *characterizing* the equilibrium. So we have

$$\frac{\partial \log K}{\partial p} = \frac{-\Delta v}{RT},$$

expressing the effect of pressure upon a chemical equilibrium.

One more case remains under this head, that concerned with the influence of temperature upon a movable equilibrium. On adding the heat-quantity Q to a chemical system, the resulting balance between it and the volume-energy change of the displaced chemical equilibrium is

$$\frac{Q}{T} \cdot dT - (\Sigma vdp - \Sigma VdP) = 0,$$

$$\frac{Q}{T} \cdot dT - RT\partial \log K = 0,$$

$$\frac{\partial \log K}{\partial T} = \frac{Q}{RT^2}.$$

This equation connects the influence of temperature with the heat of reaction. Its applications to chemical phenomena have been extended and are brilliant in the extreme.

Since the idea of chemical affinity is not always an entirely clear one, it may be in place to add a few words about it from the energy point of view. Chemical action usually effects changes in the state of aggregation or in the density of the substances concerned, and so produces work (or other energy-forms—*e. g.*, electricity—entirely convertible into work), as well as heat. A distinction must therefore be made between that part of the available energy capable of direct conversion into work and that part producible only as heat. The first is appropriately termed the *free energy*, the second the *bound energy* of the system.

A spontaneously-occurring natural process is one taking up no energy other than heat from the surrounding medium. Every such process may be made to yield a definite maximum amount of work. For, if its available work were negative it would have to take place without absorption of energy, and on being reversed by the addition of heat would transform this heat into work. The operation might be indefinitely repeated, continually converting heat of constant temperature into work, a result in conflict with the Second Law of Energy.

Since every spontaneous process must yield work, a system incapable of doing so (one whose *free energy* has minimum value) is incapable of spontaneous change—is in stable equilibrium. So this condition of equilibrium, deduced from the Second Law of Energy, is: *The decrease of free energy must be a maximum.*[1]

Processes originating spontaneously and proceeding at constant temperature can take place only in such direction as to cause a diminution of free energy, a production of energy-forms convert-

[1] Helmholtz, 1882.

ible without limit ("work"). It is therefore the decrease of free energy, and not the heat developed, which determines the direction in which chemical affinities can become active, *and which is the measure of the work-value of the chemical forces.*

Of all possible chemical changes in a material system the one involving the greatest decrease of its free energy (the maximum available work) will occur. Neither the reaction involving maximum production of heat, nor that of maximum thermal tonality (sum of heat and work produced), will necessarily take place; there are in fact many spontaneously-occurring chemical processes which absorb heat. The decrease of free energy in any given reaction is found by determining the work to be gained when the transformation is made reversible and isothermal.

An especially important feature of the energy-theory is its entire disregard of assumptions and hypotheses. In dealing directly with known facts, the results which it reaches are of necessity actual relations between measurable quantities. Among them are the remarkable relations which form the framework of thermodynamics, of electro-chemistry, of chemical equilibrium, of the solution-theory. The mutual dependence of vapor-pressure and heat, of vaporization, of electromotive force and heat of reaction, of reaction-velocity and temperature, of the freezing-point of a solution and the heat of fusion of its solvent, are among the most brilliant results of exact science. Trevor.

A Dictionary of Applied Chemistry. By T. E. Thorpe, B. Sc. (Vict.), Ph. D., F. R. S., assisted by eminent contributors. In three volumes. Vol. 3. London and New York: Longmans, Green & Co., 1893. 1058 pages. 8vo.

Vols. 1 and 2 of this very valuable work have formed the subject of notices at the time of their appearance. Both Professor Thorpe and his brother chemists are to be congratulated upon the completion of their labor. It is safe to assert that there is no better book on applied chemistry in any language, and it is essential to every chemical library. There appears to be no better way of conveying an idea of the character of the book than by giving a partial list of the important articles and their authors. The subject of Fixed Oils and Fats has been treated by A. H. Allen; Paper, by E. J. Bevan; Water, by Percy F. Frankland; Spectrum Analysis, by W. N. Hartley; Starch and Saccharimetry, by John Herron; Stearin and Commercial Stearic Acid, by G. T. Holloway; Persian Berries, Quercitron Bark, Safflower, Turmeric, Weld, and Woad, by J. J. Hummell; Phthalic Acid, Quinone and Quinones, Salicylic Aldehyde, Thiophen, Toluene, by F. R. Japp; Salts of Potassium, Sodium Sulphate, Sodium

Carbonates and Caustic Soda, by G. Lunge; Sugar, by J. A. R. and B. E. R. Newlands; Pyrotechny, by G. S. Newth; Solution, by W. W. J. Nicol; Ultramarine, by G. W. Rawlins; Phosphorus, by J. B. Readman; American Petroleum, by S. P. Sadtler; Photography, by J. M. Thomson; Essential Oils, Resin, and Terpenes, by W. A. Tilden; Triphenylmethane Coloring Matters, by Otto N. Witt; Soap, Sulphur, Sulphuric Acid, by C. R. Alder Wright; Phenol, Picric Acid, Quinoline, by W. P. Wynne; Thermometers, by Sydney Young.

The names of the authors furnish strong evidence as to the character of the book. No one person could intelligently review it. Among the articles that appeal most strongly to the general chemist are, of course, those on Water, Triphenylamine Coloring Matters, Photography, and Sodium Compounds. These are admirably written, and are good examples of what dictionary articles should be.

It is to be hoped that not many errors are contained in the work like that pertaining to the discovery of Saccharin—a small matter in itself, to be sure, but worth noting, and of some little interest, especially to the writer of this notice.   I. R.

Hand- und Hilfsbuch zur Ausfuehrung Physiko-chemischer Messungen. W. Ostwald. Leipzig: Engelmann, 1893. (8 Marks.)

In this handy little volume of three hundred pages, Ostwald has condensed the results of his extended and very exceptional experience in the practical details of the conduction of research in physical chemistry. The chapters treating glass-blowing, weighing, and the determination of solubilities and of molecular weights, contain many valuable suggestions about these ordinary manipulations of the laboratory. Those on the determination of temperatures, pressures, densities, surface-tensions, heat-quantities and critical data, together with those on optical and electrical measurements, are necessarily of more special interest. The descriptions and explanations are admirably clear, the book is practically arranged and well printed, and it is accompanied by various separately printed tables which materially enhance its practical value.   J. E. T.

NOTES

EDITOR AMERICAN CHEMICAL JOURNAL:

In the Journal for May I notice, on page 375—"Studies on the Properties of Carbon and the Preparation of Diamond"—the statement that the meteorite described by Henri Moissan was the first in which diamonds were found. This is an error. There was a meteorite which fell September 22, 1886, near Nowo Urei, Government of Pensa, Russia, and was found by M. Zerofereff and P. Latschinoff to contain one per cent. of ordinary diamond.[1]

Another instance of great interest was the discovery made by Prof. A. E. Foote, of this city, of meteoric iron containing diamonds, in the Cañon Diablo, Arizona.[2] A prospector in Arizona reported a vein of metallic iron near Cañon Diablo. This so-called vein was examined by Prof. Foote, who found, scattered over an area of over one-third of a mile, 131 small meteorites ranging in weight from 1.79 grams to 3 kilograms. Several large specimens were also found. The largest mass weighed 201 pounds, and was flattened and rectangular in shape, showing three large pits which pass through the iron. Another mass weighed 154 pounds and was also pitted. Another mass, weighing 40 pounds, was broken with a trip-hammer, and it was in this specimen that diamonds were found. It was sent to Prof. G. H. Kœnig, of the University of Pennsylvania, for analysis and examination. In cutting the meteorite it was found to be unusually hard; the section took a day and a half, and a number of chisels were destroyed. In polishing the surface to bring out the Widmannstättian figures, the emery wheel was broken; it had passed through a cavity containing diamonds which cut it through. The diamonds were both black and white. The white specimen was half a millimeter in diameter. Carbide of iron was also found in the same cavity. The meteorite contained sulphur, phosphorus, cobalt, silicon, iron and nickel; the last-mentioned amounted to but 3 per cent. The specimen described by Henri Moissan was one of those found in Cañon Diablo and was presented to the French Academy.

CENTRAL HIGH SCHOOL, PHILADELPHIA, *Nov.* 2, 1893.   OSCAR C. S. CARTER.

THE American Academy of Arts and Sciences, at a meeting held in Boston, November 8, voted to grant—from the C. M. Warren Fund for Encouraging Chemical Research—the sum of $300 to Professor C. F. Mabery of Cleveland, Ohio, in aid of his Investigations on the American Sulphur Petroleums.

[1] Am. J. Sci. [3] **36**, 74.   [2] *Ibid.* [3] **42**, 413

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